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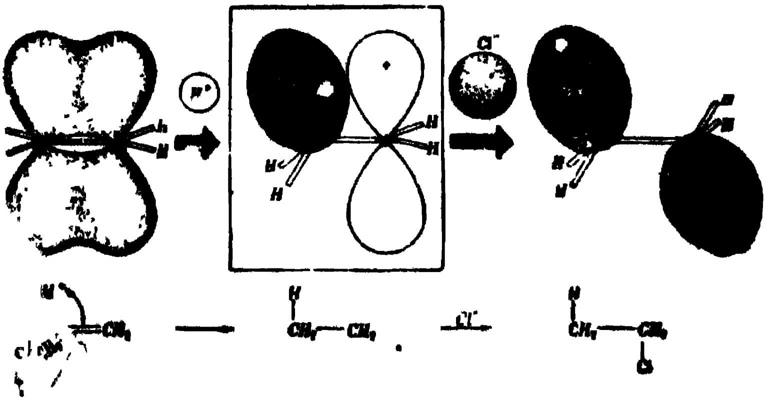
VOLUME ONE

Part I—General

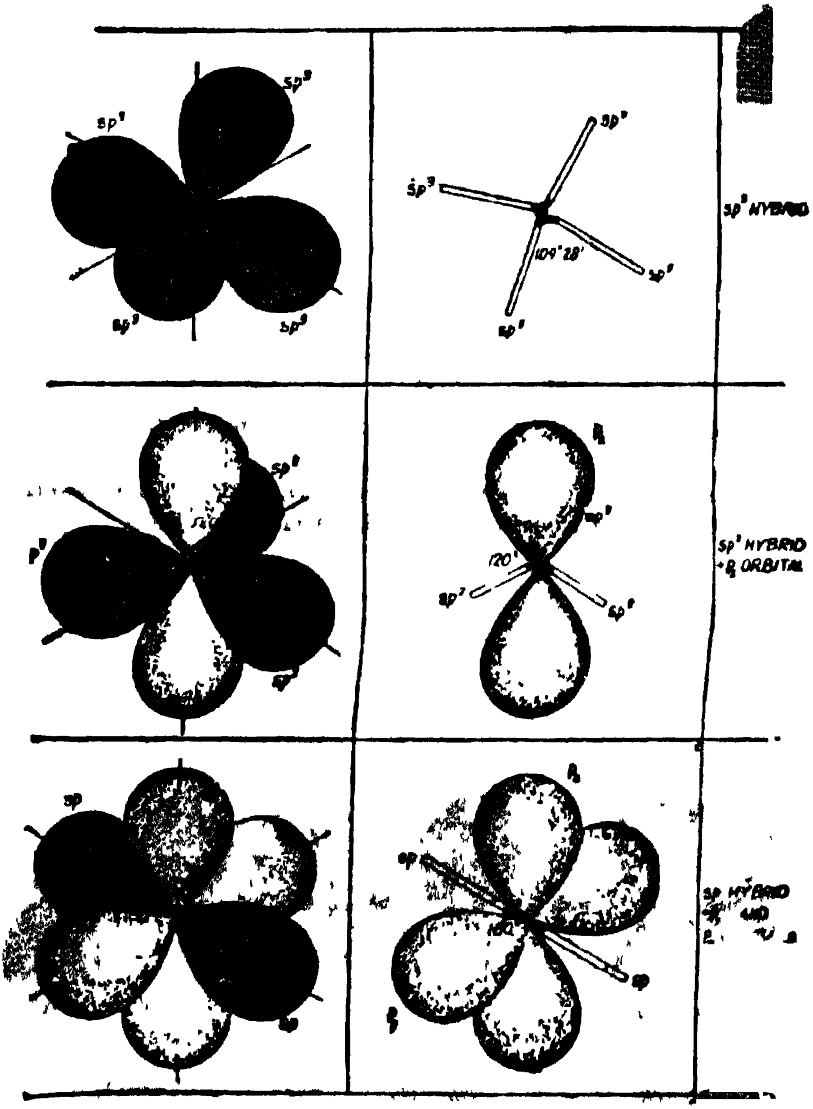
Part II—Aliphatic Compounds, Alicyclic Compounds

Appendices—Typical Numerical Problems, Typical Conversions, Miscellaneous Questions, New Type Question Bank.



orbital representation of the reaction of hydrogen chloride and ethylene. Filled orbitals are shaded empty orbitals are unshaded.

Hybrid Orbitals



The three important hybrids of 2s and 2p orbitals. [illegible] *The sp^3 hybrids are used in saturated molecules, the sp^2 hybrid are found in alkenes and sp hybrids in alkynes.*

1

Introduction

1. **Origin of Organic Chemistry.**—The name *organic* dates ack to the time before 1828 when all those compounds, which were btained from plants or animals, that is, from living *organisms*, were called organic compounds. Organic chemistry deals with the study of these organic compounds. The study of chemical compounds aving a mineral origin such as common salt and sulphur, is termed Inorganic Chemistry. It was Lavoisier (1743-1794) who showed that nearly all substances of plant origin are composed of *carbon, hydrogen* and *oxygen*. Organic compounds of animal origin also consist of the same three elements but frequently contain *nitrogen* and sometimes *sulphur* and *phosphorus* also.

2. **The Vital Force Theory.**—This similarity in composition of organic compounds and the fact that they behave differently from inorganic compounds, in being combustible, led Swedish chemist *Berzelius* (177 -1846) to believe that some *vital force* (*life force*) was necessary to produce organic compounds and an artificial preparation of these was impossible due to the absence of this vital force in the test tube. The mysterious force, inherently present in the body of the living organisms, was responsible for the synthesis of organic compounds there. The vital force theory, put forward by Berzelius, has no scientific background but held the field till 1828, when a German nist, Friedrich Wohler (1800-1882), working in Heidelberg, ported that upon treating lead cyanate with ammonium hydroxide, he obtained urea. Since urea was a well known organic compound ving been isolated from human urine by Roulle in about 1780, hler had prepared an organic compound in the laboratory for the first time.

$$\underset{\text{Lead cyanate}}{Pb(CNO)_2} \xrightarrow{NH_4OH} \underset{\text{Ammonium cyanate}}{NH_4CNO} \xrightarrow{\text{Heat}} \underset{\text{Urea}}{NH_2.CO.NH_2}$$

Although the synthesis of urea was recognized by the leading chemists of the day, the concept of vitalism did not die quickly. It was nly after Kolbe had synthesised acetic acid in 1845 and Berthelot ad synthesised methane in 1856 that the belief in vital force theory as abandoned. Thus we see that the vital force theory died only a lingering death.

3. **Organic Chemistry Defined.**—The so-called organic mpounds have been found to be mainly compounds of carbon d hydrogen (called hydrocarbons) or their derivatives. Therefore, **Organic Chemistry** is defined today *as the chemistry of drocarbons and their derivatives*

There is at present no sharp line of demarcation between organic and inorganic chemistry. If the distinction between organic and inorganic compounds is being still retained, it is more a matter of convenience than of principle.

Various reasons for treating organic chemistry as a separate branch of the subject. The following characteristics of organic compounds justify the treatment of organic chemistry as a separate branch of the subject:

(*i*) **Their large number.** Compared with the compounds of other elements, the number of organic compounds is very large. About one million organic compounds are already known and more are being added to the list. This is due to the peculiar property of the carbon atom to combine with itself and form long chains. This property of carbon atom is called *catenation*. It is not possible to include all these carbon compounds in the chapter on carbon in any textbook.

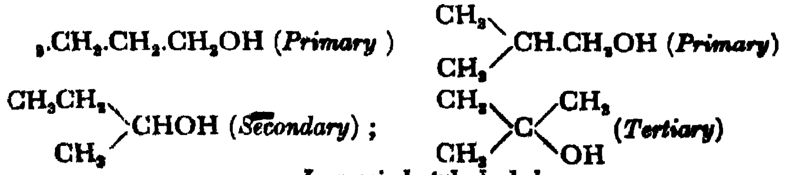
(*ii*) **Complexity of molecules.** Certain organic molecules are usually more complex and, therefore, possess a higher molecular weight than inorganic molecules. For instance, molecular weights of proteins (organic compounds) range from several thousands to over a million.

(*iii*) **Their non-ionic character.** Organic compounds are generally covalent compounds and do not, therefore, ionize when dissolved in water. For example, chloroform ($CHCl_3$) gives no white precipitate with silver nitrate solution (a characteristic property of inorganic chlorides). Their covalent nature also accounts for their low melting and boiling points and tendency for decomposition on heating, etc.—*their comparative instability.*

Inorganic compounds, on the other hand, usually ionize in solution and are comparatively more stable. Inorganic reactions are mainly ionic reactions. For example, all chlorides give white precipitate with silver nitrate solution—a property of the chloride ions.

$$KCl \rightleftharpoons K^+ + Cl^-$$
$$AgNO_3 \rightleftharpoons Ag^+ + NO_3^-$$
$$Ag^+ + Cl^- \rightarrow AgCl \text{ (\textit{white ppt.})}$$

(*iv*) **Isomerism.** Very often more than one organic compounds are represented by the same molecular formula. For example, $C_4H_{10}O$ stands for four butyl alcohols as given below and three ethers, viz., $C_2H_5—O—C_2H_5$, diethyl ether, $CH_3—O—CH_2.C_2H_5$, methyl *n*-propyl ether, and $CH_3—O—CH(CH_3)_2$, methyl *iso*-propyl ether.



$_3.CH_2.CH_2.CH_2OH$ (*Primary*)

$(CH_3)_2CH.CH_2OH$ (*Primary*)

$(CH_3CH_2)(CH_3)CHOH$ (*Secondary*) ;

$(CH_3)_3C.OH$ (*Tertiary*)

Isomeric butyl alcohol

Various organic compounds represented by the same molecular formula are called ***Isomerides*** *while the phenomenon is known as*

Isomerism. The different properties of each one of the isomers are due to difference of arrangement of atoms.

In inorganic chemistry one molecular formula stands for only one compound, *e.g.*, H_2SO_4 stands for sulphuric acid and nothing else.

(*v*) **Polymerism**. It is the existence of two or more compounds having the same empirical formula, the molecular formula of one being some simple multiple of that of the other, *e.g.*,

$$\underset{\text{Acetylene}}{C_2H_2} \quad \text{and} \quad \underset{\text{Benzene}}{C_6H_6}$$

Quite a few organic compounds exhibit polymerism but inorganic compounds do not.

(*vi*) **Homologous Series**. Organic compounds are classified in groups or families known as *Homologous Series*. Different members belonging to a certain homologous series called *homologues* are characterised by the presence of a *characteristic group* and can be represented by a *general formula*. The common difference between consecutive members of the series is CH_2. They can be prepared by general methods of preparation and possess similar chemical properties with a regular gradation in their physical properties. This has reduced the study of over a million organic compounds to the study of a few homologous series. Similar properties of different homologues are the properties of the characteristic group or the functional group present in each one of them.

(*vii*) **Rate of Organic Reactions**. Reactions between organic compounds are slow in most of the cases due to their being reversible and invariably accompanied by the side reactions. This is also because they represent the activity of the molecules rather than ions. They never proceed to completion and their yield is generally low.

(*viii*) **Their Structure**. The structure (arrangement of atoms in the molecule) of most organic compounds is well established. It is more difficult to determine the structure of inorganic compounds and comparatively very few of them have been completely worked out.

(*ix*) **Solubility**. Organic compounds, unlike inorganic compounds, are mostly insoluble in water. They are, however, soluble in organic solvents, *e.g.*, alcohol, ether, benzene, etc., in which most of the inorganic compounds do not dissolve.

(*x*) **Origin**. In comparison with the inorganic compounds, which have a mineral origin, organic compounds are mostly obtained from animal or vegetable kingdom.

4. **Rise of Organic Chemistry.**—After the discoveries of Wohler (1828), Kolbe (1840s) and R 50s), chemists recognised that it was not th rted uniqueness to organic chemistry but rath ganic compounds were all compounds of carl began to take on new dimensions as the tech nalysis of carbon and hydrogen was perfecte accurate formulae were available for a goo plicated organic compounds. Various theo in order to explain complexities such as isomerism, substitution, etc.

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In 1852 Frankland advanced the concept of valence. In 1858 Kekule and Couper proposed that carbon atom is always tetravalent and that carbon atoms have the ability to link with each other. In 1858 Cannizaro used Avogadro's hypothesis in the determination of accurate molecular weights of organic compounds. Knowing accurate molecular weights, chemists started thinking in terms of molecular structure and the chemical bond. Kekule introduced the idea of a bond between atoms.

Organic chemistry has now matured as a scientific discipline. Over 95% of the known chemical compounds are organic compounds and half of the present-day chemists are organic chemists. Rapid advancement in the field of organic chemistry is due to the fact that organic chemical industry plays a major role in world economy and because organic chemicals are literally the "stuff of life." Majority of the important discoveries by chemists in the recent past have been discoveries in organic chemistry.

5. **Why Study Organic Chemistry?**—In most of the chemical industries around us we encounter organic reactions. So if you want to be a chemical engineer, organic chemistry will be a part of your life. Chemotherapy is one of the major techniques in modern medicine and majority of the modern life-saving drugs are organic compounds. If you happen to be a doctor, you will be surrounded by these organic compounds throughout your life. You may be intending to specialise in biochemistry, molecular biology or any other life science. A good background of organic chemistry is essential for each one of these. Biochemistry is simply a study of organic chemistry related to living organisms. Similarly, the molecules of molecular biology are organic molecules. You may be intending to specialise in some other area of chemistry and may need the knowledge of organic chemistry related to your speciality area.

Apart from these vocational motivations, study of organic chemistry is an extremely stimulating intellectual pursuit. It has a highly logical structure and its study promotes logical thinking.

6. **Organic Chemistry in the Service of Mankind.**—Our body is made up of tissues which are all composed of organic substances. To maintain health we need an adequate supply of organic compounds, *e.g.*, food, vitamins, hormones, enzymes, etc. Study of life processes, like digestion and assimilation, is nothing but a study of organic chemistry. Miracles of modern science like the change of sex are outcome of the study of sex hormones by the organic chemist.

An idea of the use of organic compounds in the service of mankind can be had from their application in everyday life as given below:

Foods—Starch, sugar, fats, vitamins, proteins.

Fuels—Wood, coal, alcohol, petrol.

Household and commercial articles—Paper, soap, cosmetics, oils, flavouring essences, photographic developers, dyes, paints, varnishes, inks.

Textile fabrics—Cotton, wool, silk and linen (natural products), rayon, nylon (synthetic products).

Drugs and disinfectants—Penicillin, quinine, aspirin, chloroform, iodoform, carbolic acid, lysol, sulpha drugs.

Poisons—Opium, strychnine

Perfumes—Vanillin, camphor, ionone.

Explosives—Nitroglycerine, dynamite, picric acid, TNT.

Dyes—Indigo, congo red, malachite green, etc.

War gases—Mustard gas, chloropicrin, lewisite.

We find that organic compounds penetrate into every phase of our life. We look to and count on an organic chemist for the manufacture of the above compounds and for the development of various chemical industries—paper, sugar, starch, vegetable oils, vegetable ghee, essential oils, tannery, distillery, soap, cosmetics, rubber, dyestuffs, plastics, petroleum, etc.

QUESTIONS

Essay Type :

1. Give a brief account of the rise, development and characteristics of organic chemistry.

2. How do you define organic chemistry ? How would you justify the treatment of organic compounds as a distinct branch of chemistry ?

3. Write a short note on "Organic Chemistry in the Service of Mankind".

Short Answer Type :

1. What is vital force theory ? How was it abandoned ?

2. What is isomerism ? Which different compounds are represented by the formula $C_4H_{10}O$?

3. What is the importance of organic chemistry to a doctor specialising in modern medicine.

4. Name ten organic substances which you come across at home or while coming to the college.

Purification of Organic Compounds

1. **Introductory.**—Most of the organic compounds occur together at one source and many of them have similar chemical and physical properties. A large number of them decompose on heating, are sensitive to other reagents and resist the solvent action of water ; so the separation of organic compounds in a pure state from their natural sources involves laborious or elaborate processes depending upon their class properties and nature of the impurities present.

In the chemical investigation and characterisation of an organic compound, whether natural or artificial, a complete molecular diagnosis is necessary. For this purpose before subjecting an organic compound to qualitative or quantitative analysis, it must be obtained in a pure state. All organic chemicals, medicines and utility compounds must be purified thoroughly before they are put on the market. Hence, purification of organic compounds, though tedious, is an indispensable operation.

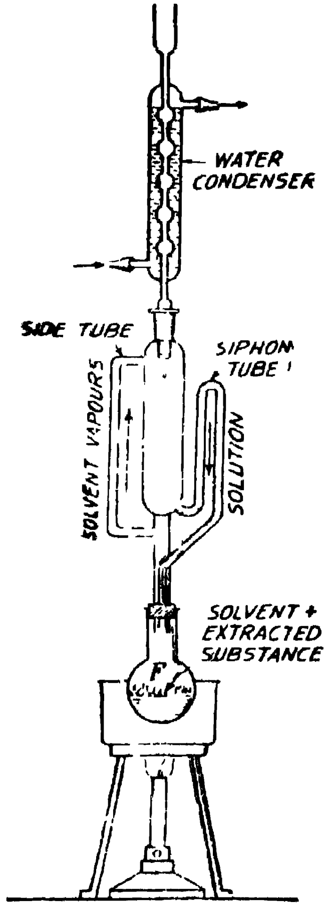

Fig. 2·1—Soxhlet apparatus.

2. **Extraction of Organic Compounds.**— Certain organic compounds are present in certain plants or flowers. These can be extracted from their natural sources with suitable solvents. The source material is heated with hot solvent in a flask or Soxhlet apparatus (Fig. 2·1). Alkaloids, essential oils of flowers and leaves, vegetable colouring matter of leaves and soluble constituents of certain roots can also be extracted very easily with a suitable solvent in the Soxhlet apparatus. The soluble constituents pass in solution and are separated by simple or fractional crystallization.

The Soxhlet apparatus in its essentials consists of a *wide tube* provided with a *side tube* on the left, a *siphon tube* on the right and a *water condenser* at the top. The herbs or flowers are placed in the wide tube and the apparatus is fitted in the neck of a flask *F* containing a suitable solvent.

The solvent in the flask *F* is boiled, the vapours of the solvent find their way through the side tube into the water condenser where they get condensed.

The droplets of the condensed hot solvent fall on the mass placed in the wide tube and dissolve out the soluble constituents from it. The level of the solution goes on rising till the siphon begins to work and the solution passes through the siphon tube back into the flask *F*. The process continues and more and more of the soluble constituent passes in solution collected in *F*. The solid is then separated as usual by crystallization from the solution obtained above.

3. **Methods for Purification of Solids.**—The common methods employed in organic chemistry for purification of solid substances are enumerated below :

(1) **Crystallization.** Of the vast number of organic compounds now known, the majority of the purely synthetic ones and large number of the natural products are crystalline. These are purified by crystallization from a suitable solvent which can dissolve a large quantity of the substance at high temperature and deposit the same when cooled.

A nearly saturated solution of the impure substance is prepared in hot. It is decolorised with bone charcoal, if necessary, and filtered while hot preferably through a hot water funnel (Fig. 2·2). A hot water funnel is an ordinary funnel surrounded by a copper jacket containing hot water. This prevents cooling and consequent crystallization of the solid over the filter paper during filtration. Care is taken that solvent vapours do not catch fire by coming in contact with the flame. The filtrate on being allowed to cool slowly in a shallow basin deposits crystals of the pure substance. These can be further purified by recrystallization and dried over a filter paper, a porous plate and finally in a desiccator.

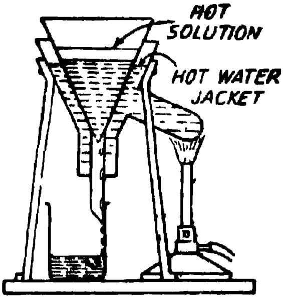

Fig. 2·2—Hot water funnel.

Expt. 1. Prepare a hot saturated solution of benzoic acid in water. Filter

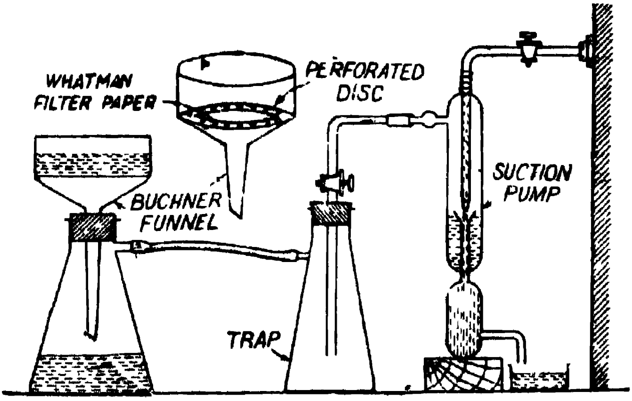

Fig. 2·3—Filtration with suction.

while hot through a hot water funnel and allow to stand. Glistening plates are deposited on cooling.

The crystals are conveniently washed on a Buchner funnel (Fig. 2·3), the filtration and draining is accelerated by the use of water pump. A centrifuge is often used in technical operations for rapid separation of crystals from the mother liquor.

(2) **Fractional crystallization.** If the impure substance is a mixture of two substances *A* and *B* both soluble, the less soluble *A* will crystallize out first from a saturated solution and may be contaminated with a little of *B*. The mother liquor on further concentration will deposit crystals of *B* contaminated with *A*. The process is repeated several times to get pure samples of *A* and *B*. This is called *Fractional Crystallization*.

NECESSARY MODIFICATIONS

(*a*) *Crystallization by spontaneous evaporation.* In case no suitable solvent is available and the given substance is as soluble in cold as in hot solvent, crystallization is carried out by spontaneous evaporation. A concentrated solution is prepared and allowed to evaporate slowly. As a solvent evaporates, the solution gets more and more concentrated and finally results in the separation of crystals.

(*b*) *Use of miscible solvents.* If the given substance *X* is very soluble in solvent *A* and very sparingly soluble in another solvent *B*, both these solvents are unfit for use in crystallization.

In case *A* and *B* are miscible and *B* has higher boiling point than that of *A*, their mixture proves to be useful for the purpose. A concentrated solution of *X* is prepared in the solvent *A* and then solvent *B* is gradually added to solution till a slight turbidity occurs. The turbid solution is allowed to cool when crystals are obtained. For example, *m*-dinitrobenzene is more soluble in alcohol than in water. As evaporation of *m*-dinitrobenzene in dilute alcohol proceeds, more and more of alcohol evaporates leaving the solution richer in water and crystals of *m*-dinitrobenzene are obtained.

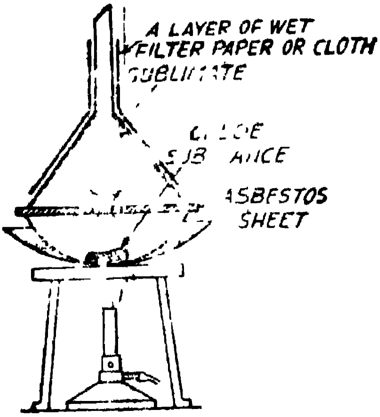

Fig. 2·4—Sublimation.

Pairs of miscible solvents frequently employed for the purpose are :

(*i*) Alcohol+water ;
(*ii*) Alcohol+ether ;
(*iii*) Benzene+petroleum ether ;
(*iv*) Chloroform+petroleum ether.

(3) **Sublimation.** Certain organic compounds sublime on heating, *i.e.*, pass directly from solid to vapour state on heating and *vice versa* on cooling, *e.g.*, naphthalene, anthracene, camphor, and indigo.

$$\text{Solid} \underset{\text{Cooling}}{\overset{\text{Heating}}{\rightleftharpoons}} \text{Vapour}$$

The process is known as sublimation and is found very useful in separating substances which sublime on heating from non-volatile impurities or *vice versa*.

The impure substance is heated in a dish covered with a perforated asbestos sheet on which an inverted funnel is placed (Fig. 2·4). The funnel is kept cool by wrapping it with a wet filter paper or wet cloth. Vapours of the substance rise up and condense on the cooler walls of the funnel.

Expt. 2. Mix a little of anthraquinone with some common salt Heat it in a dish covered with a perforated asbestos sheet and an inverted funnel. Pale yellow needle-shaped crystals of anthraquinone are deposited on the cooler sides of funnel while common salt is left behind.

Substances which decompose at their sublimation temperature are purified by sublimation under reduced pressure in the apparatus shown in Fig. 2·5.

It consists of two tubes one fitting into the other. Impure substance is placed in the outer tube which is connected to a vacuum pump. Inner tube is fitted with two glass tubes, one brings in cold water and the other acts as overflow. On heating the outer tube the substance vaporises and then condenses on the cooler outer surface of the inner tube.

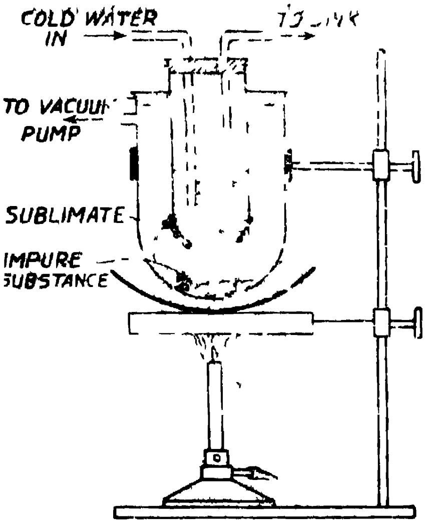

Fig 2·5—Sublimation under reduced pressure.

4. Methods for Purification of Liquids.—Various methods employed for the purification of liquids, depending on the nature of the liquid and the nature of impurities present. are ·

(1) **Simple distillation.** Liquids which boil under ordinary pressure without decomposition and are associated with non-volatile impurities are generally purified by simple distillation. It is a process in which vaporization and condensation are going on side by side. The impure liquid is taken in a distillation flask fitted with a thermometer and a condenser and heated on a wire gauze. The liquid vaporizes and the vapours are condensed as they pass through the air or water condenser. The pure liquid is collected in the receiver while the non-volatile impurity is left behind. Some glass beads are generally added to the distillation flask to avoid bumping.

(2) **Fractional distillation.** The liquids are freed from their volatile impurities by *Fractional Distillation*. When the mixture of two liquids, *A* and *B*, is heated in a distillation flask the low boiling constituent *A*, contaminated with a little of high-boiling constituent *B*, distils over first and is collected separately. The two fractions are further purified by repeating the above separations a number of times.

To decrease the number of distillations or to separate *A* and *B*, when their boiling points are very near to each other, a fractionating column is used. It is a long tube provided with obstructions to the passage of the vapours upwards and that of the liquid downwards.

The liquid mixture to be fractionated is placed in a distillation flask, fitted with a fractionating column, a thermometer and a condenser as shown in Fig. 2·6. The flask is heated from below. The liquid vaporizes and the vapours rise into the fractionating column where some of them condense and start flowing down.

At each obstruction in the fractionating column there occurs, an exchange of constituents between the up-going vapours and the down-coming liquid. The vapours lose more and more of the high-boiling constituent B, by condensation as they rise up and the liquid loses more and more of low-boiling constituent A by evaporation. Thus pure A passes at the top and pure B remains in the flask below.

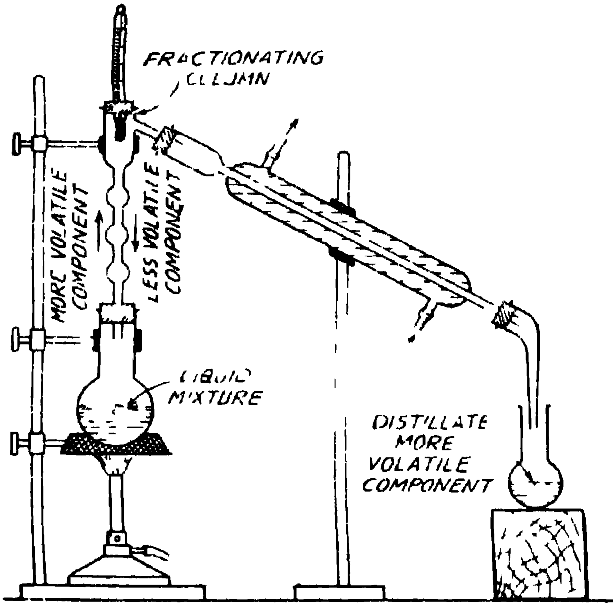

Fig. 2·6—Fractional distillation.

Fractional Distillation in Industry. On a commercial scale, fractional distillation is done in carefully designed big fractionating columns, e.g., in petroleum refineries, distilleries. One such column is shown in Fig. 2·7. It is about 10 m high and even more in certain cases.

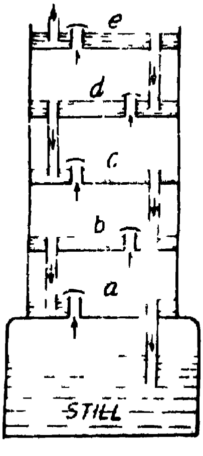

Fig. 2·7—Bell and plate type fractionating column.

There are bells and plates provided at different heights which divide the column into different compartments. The mixture is heated in the still at the bottom. The vapours from the still enter compartment a and get partially condensed. The condensate rich in high-boiling constituent collects on the plate and more volatile components pass on into the next compartment b. Thus the vapours travel upwards from one compartment to the other. The liquid flows down and falls from one compartment to the one next below through overflow pipes.

Vapours of the low-boiling constituents escape at the top and are condensed while the high boiling point fraction collects at the bottom and is withdrawn from time to time.

(3) **Distillation under reduced pressure.** Most of the organic compounds decompose when heated to their boiling points, glycerine is a common example. Such substances cannot be purified by simple distillation.

Boiling point of a substance is the temperature at which the vapour pressure of the liquid is equal to the atmospheric pressure This means that by lowering the pressure to which a liquid is subjected the boiling point of the liquid can be lowered. Similarly by raising the pressure, we can raise the boiling point. Thus we notice that a liquid can be made to boil at any temperature by changing the pressure.

Now if we have an organic substance which decomposes at its boiling point, we make it boil, so to say, at a temperature before it can decompose. All that we have to do is to create a partial vacuum. Under reduced pressure, the substance boils at a much lower temperature and distils over undecomposed.

Distillation under reduced pressure or vacuum distillation, as it is generally called, is carried out in a specially designed apparatus (Fig. 2·8). The receiver is attached to a vacuum pump to lower the pressure registered by the manometer provided, and the distillation carried out as usual.

Distillation under reduced pressure is not only useful in avoiding decomposition but also serves to economise fuel for industrial concerns. For example, in sugar factories, raw juice is concentrated by heating under reduced pressure in specially designed vacuum pans. Liquid mixtures, which would otherwise boil at inconveniently high temperatures, are separated into their constituents by vacuum distillation.

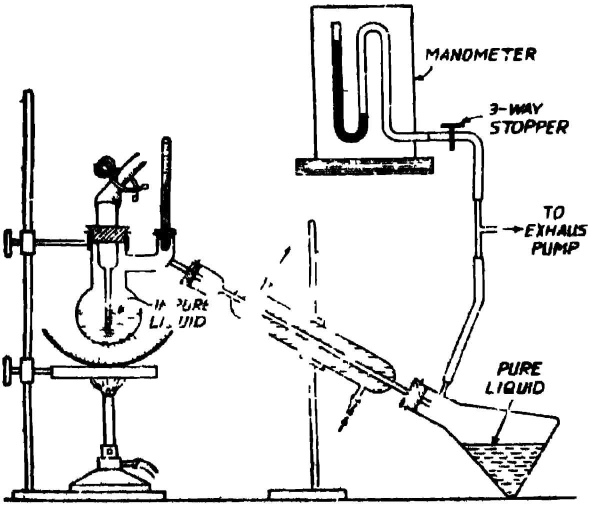

Fig. 2·8—Distillation underd reduce pressure.

(4) **Steam distillation**. Liquids practically immiscible with water, volatile in steam and possessing a fairly high vapour pressure, *e.g.*, aniline, are purified by steam distillation

Steam is bubbled through the impure liquid in a flask heated on a sand bath (Fig 2 9 Vigorous boiling sets in and vapours of the organic substance mixed with steam rise up and condense as they pass through the water condenser Thus the condensate is a mixture of the organic substance and water The two being immiscible are separated in a separating funnel (Fig 2 10) In case the organic compound is partially miscible with water, it is extracted with a suitable solvent Pure organic compound is then recovered from the extract by fractional distillation

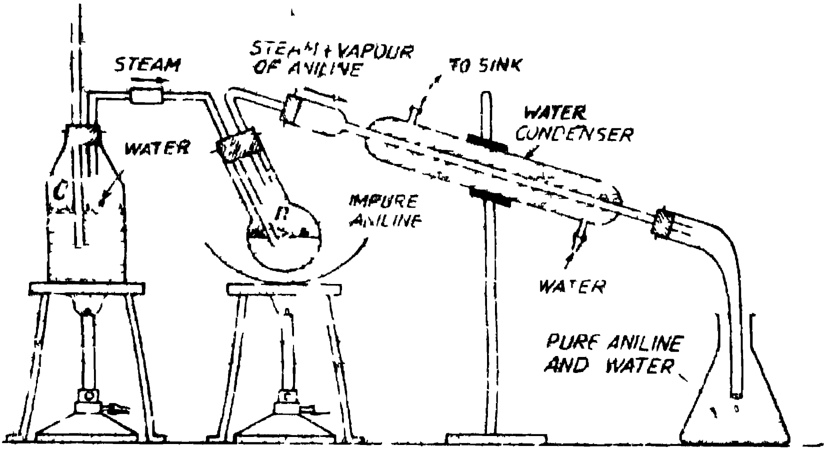

Fig 2 9—Steam distillation

Theory of Steam Distillation Let p_1 and p_2 be the vapour pressures of water vapour and liquid at the distillation temperature The liquid boils when their sum is equal to the atmospheric pressure, P, *i e*,

$$p_1 + p_2 = P \qquad \text{or} \qquad p_2 = P - p_1$$

It is evident that when a liquid boils in the presence of steam, p_2, the partial pressure of organic liquid, is less than the atmospheric pressure, *i.e.*, the substance is boiling under somewhat reduced pressure, p_2 at a temperature lower than its boiling point. Thus the principle is similar to distillation under reduced pressure.

The actual amount of the substance which distils over is given by the relation :

$$\frac{W_1}{W_2} = \frac{p_1 \times 18}{p_2 \times M}$$

where W_1 = Weight of water which distils over,
W_2 = Weight of the substance which is carried over,
p_1 = Vapour pressure of water vapour,
p_2 = Vapour pressure of the substance,
18 = Mol. wt. of water,
and M = Mol. wt. of the substance.

(5) **Extraction with a solvent.** The impure liquid is freed from a miscible impurity by shaking it in a separating funnel with a suitable solvent which can dissolve one of the constituents *A* and is immiscible with the other constituent *B*. The two are separated in the separating funnel and *A* is separated from the solvent by distillation. Miscible liquids which cannot be separated by distillation and a volatile solid from its solution are also generally separated by extraction with a suitable solvent which dissolves one of the constituents and yet remains immiscible with the other constituent.

Expt. 3 Take alcohol and water in two test tubes. Add benzene to either and show that benzene is miscible with alcohol and immiscible with water. Take the alcohol-benzene mixture in a separating funnel and shake with excess of water. The liquid separates into two layers after a while. Run off the bottom layer of aqueous alcohol and repeat the process to extract the remaining traces of alcohol from the upper benzene layer.

According to Partition Law, it is better to repeat the process of extraction with smaller amounts of the solvent. For example, the substance extracted in five lots with 10 ml of the solvent each time is definitely more than extracted with 50 ml of the same solvent in one lot.

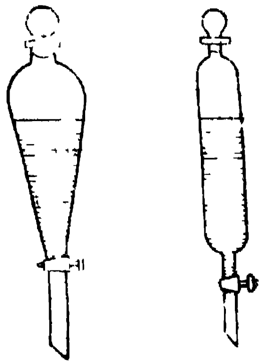

Fig. 2·10—Separating funnels

(6) **Salting out.** Many organic compounds, *e.g.*, ethanol acetone, pyridine, etc., which are soluble in water are either insoluble or sparingly soluble in solutions of salts like common salt, calcium chloride and sodium sulphate. Hence on adding the solid salt to an aqueous solution of, say aniline, it is thrown out of solution and can be separated with the help of a separating funnel or better still is extracted with ether.

Salting out of soap or sodium benzene-sulphonate by adding common salt is due to *common ion effect*. Addition of common salt increases the sodium ion concentration whereby the solubility product of sodium stearate (soap) is exceeded and it gets precipitated.

(7) **Counter-current distribution.** Counter-current distribution is an automatic procedure used for separating two closely related solutes and is based upon their slightly different partition coefficients in two immiscible liquid solvents. The technique is used when other methods such as distillation are inadequate.

About 100 to 200 identical test tubes are taken and the heavier solvent is placed in each of them. The sample is dissolved in a portion of the lighter solvent and added to test tube 1. It is shaken and allowed to settle. The upper solvent is then transferred to test tube 2 while a new portion of lighter solvent is added to test tube 1. The process is repeated with test tubes 2, 3, 4 and so on.

Suppose the sample is a mixture of solutes *A* and *B* and component *A* is more soluble in the lighter solvent as compared with the solute *B*. In every test tube partition of the two solutes takes place. More of component B passes into the lower layer and more of A is retained in the upper layer. Solute A is thus transferred from tube to tube in slightly greater amounts than B and after a number of operations would leave component B behind.

(8) **Chromatography**. It is a modern technique employed for concentrating a compound which occurs naturally in great dilution and has proved to be an extremely valuable method for the separation, isolation, purification and identification of the constituents of a mixture.

It depends on the distribution of the mixture between two phases, one fixed and the other moving. Different constituents migrate, therefore, at different rates through the fixed phase. The mixture is dissolved in the moving phase and passed over the fixed phase which may be an adsorbent column or a paper strip. The moving phase may be a liquid or a gas. Based on the nature of the fixed and the moving phase, different types of chromatography are :

(*i*) *Adsorption chromatography*. In this the fixed phase is a solid, *e.g.*, alumina, magnesium oxide, silica gel, etc. The solutes are adsorbed in different parts of the adsorbent column. The adsorbed components are then eluted by passing suitable eluents (solvents) through the column.

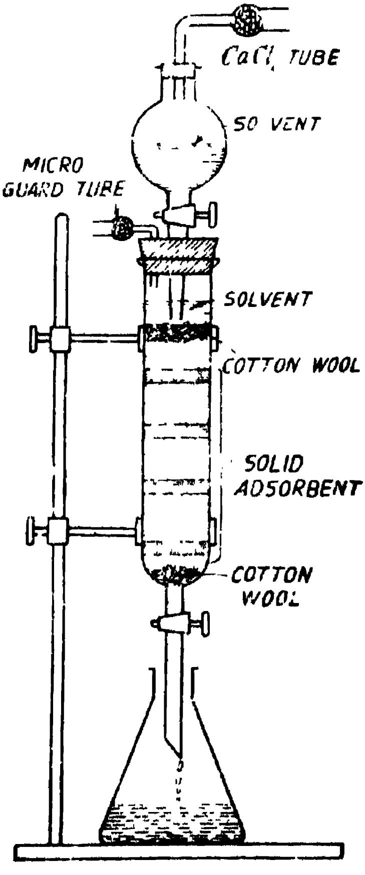

Fig. 2·11—A simple chromatographic column.

Thin layer chromatography (TLC) is a particular case of adsorption chromatography in which we use a glass strip coated with a thin layer of the adsorbent.

(*ii*) *Partition chromatography*. It operates by a mechanism analogous to counter-current distribution. The fixed phase may be a liquid strongly adsorbed on a solid which acts as a support. In this case the solute gets distributed between the fixed liquid and the moving liquid (solvent). The technique is called partition chromatography.

Paper chromatography is a special case of partition chromatography in which the adsorbent column is a paper strip.

(*iii*) *Gas chromatography*. When the moving phase is a mixture of gases it is called gas chromatography or *vapour phase chromatography* (VPC). Depending upon the nature of the stationary phase whether solid or solid coated with non-volatile liquid it is termed *gas-solid chromatography* (GSC) or *gas-liquid chromatography* (GLC).

(*a*) **Adsorption chromatography.** This method is based on the differential adsorption of the different constituents of a mixture on various adsorbents like magnesium oxide, alumina, cellulose powder, silica gel, active animal charcoal, inulin, sucrose, bentonite, kieselguhr, etc. This is useful in concentration of naturally-occurring dilute solutions and is extremely valuable for isolation or purification of an organic compound or separation of the constituents of a mixture.

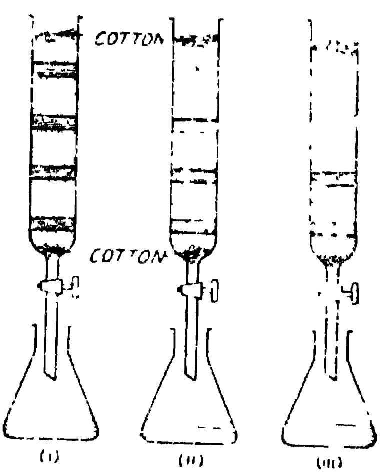

Fig. 2·12—(*i*) Chromatogram ; (*ii*) and (*iii*)—Downward movement of the bands during elution.

A long glass tube with a stop-cock at the lower end is packed with a suitable adsorbent. For this purpose the adsorbent is shaken with the solvent to be used for dissolving the mixture and the slurry obtained poured in the glass tube. The adsorbent settles down gradually and forms a column while the solvent is allowed to flow down through the stop-cock.

A concentrated solution of the mixture in a suitable solvent is adsorbed in a suitable quantity of the adsorbent and dried. This dried adsorbent is placed as top layer in the adsorbent column obtained above. Pure solvent is taken in the dropping funnel and is poured slowly at the top of the column. As the solvent passes through the top layer, it dissolves the mixture adsorbed in this layer. The solution so obtained flows down. As the solution runs through the adsorbent, the components of the mixture are subjected to a competition between the two phases. *The stationary phase (adsorbent) tries to adsorb the components on its surface while the moving phase (solvent or eluent) tries to take away the components along with it downwards.*

Different constituents of the mixture give different responses to these competing phases. The result is that the different components are adsorbed at different heights. The layers of the adsorbent with different constituents adsorbed in them are called *zones* or ***bands***. Zones possess different colours generally. Most strongly adsorbed constituent is present in the band near the top while the least readily adsorbed constituent is to be found in the band near the bottom [Fig. 2·12 (*i*)].

Extraction of the individual components from these bands. Pure solvent is now added from the top. This causes each band representing each component to travel down the column [Fig. 2·12 (*ii*) and (*iii*)]. ***This process of washing the column with pure solvent is known as Elution.***

The solutions flowing down through the stop-cock with each band disappearing are collected separately in different receivers. These are concentrated and crystallised to recover the solid component. In cases where bands do not separate completely, the solutions obtained by elution are passed through such column again.

Sometimes the adsorbent column is pushed out of the tube by tapping and cut into sections, each section carrying one band. The constituent present in each section so cut is extracted with a suitable solvent followed by concentration and crystallisation of the solution.

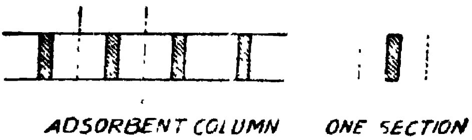

Fig. 2·13—Cutting of the adsorbent column into sections.

(*b*) **Paper chromatography**. Paper chromatography proceeds by a mechanism which is partly partition and partly adsorption. Solute mixture, generally dissolved in water, is placed on a strip of chromatographic paper and a second solvent is allowed to travel along the strip. Here cellulose of filter paper acts as support for the stationary phase, water adsorbed in it. The mixture is subjected to partition between the stationary phase (water) and the moving phase (solvent). The role of cellulose can be compared to that of separating funnel. As a result of continuous and repeated partitioning the rate of migration of each component is different, which is responsible for their separation on the paper.

Paper chromatography is mainly used for the separation of amino acids, carbohydrates, etc.

(*a*) **Radial Paper Chromatography**. In Fig. 2·14 a thin strip is cut along the radius of a circular filter paper. The thin strip is termed wick or tongue. This is placed over a petri dish containing the solvent and the strip dipping in this solvent. Solute mixture is placed at the centre of the filter paper. This is covered with a glass plate to prevent evaporation of solvent. Solvent is constantly rising up through the strip due to capillary action. This dissolves the solutes and the solution travels through filter paper. Due to differential adsorption different ingredients travel through different distances and separate in the form of semi-circular bands This is termed *Radial paper chromatography*

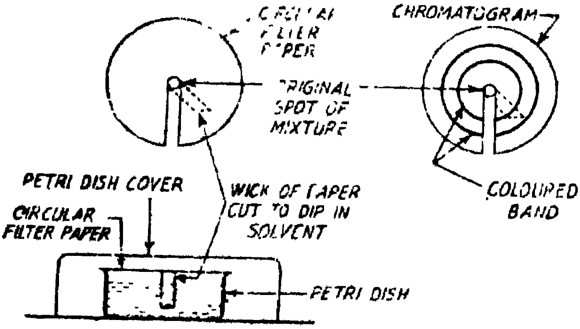

Fig. 2·14 – Radial paper chromatography.

(*b*) **Ascending Paper Chromatography.** In another arrangement for separation by chromatography, we use a filter paper strip as shown in Fig. 2·15. In a rectangular box a filter paper sheet is suspended from a glass rod. The lower edge of the filter paper sheet is dipping in a suitable solvent (eluting solvent). The front of the box is a glass window and its top is covered by a glass plate. Suppose the mixture is suspected to contain five ingredients (*A*, *B*, *C*, *D* and *E*). Mark six points on the filter paper sheet in a row. The mixture is put on one point and known samples of *A*, *B*, *C*, *D* and *E* are placed on the remaining five points. Since the lower end of the filter paper sheet is dipping in the eluting solvent, the solvent rises up due to capillary action, dissolves the sample on its way and travels up.

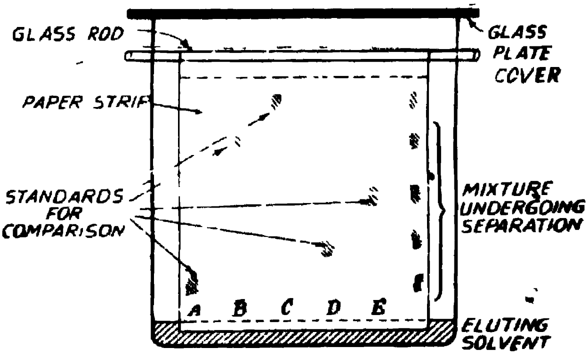

Fig. 2·15—Ascending paper chromatography.

Different ingredients of the mixture travel through different heights and correspond to the heights travelled by known samples. The constituents of the mixture are separated as well as identified.

In this case, since the eluting solvent is moving upward, it is termed *ascending paper chromatography*. Sometimes the eluting solvent is placed at the top and the upper end of the filter paper dips in it. Here the solvent moves downwards. Chromatography in this case is termed *descending paper chromatography*. Sometimes the constituents do not produce coloured bands. In such cases at the end of the test, the paper is sprayed with a special reagent to make the sample visible.

For rapid separations where identification of the components of a mixture is all that is required, paper chromatography is usually the most convenient.

R_F Values. The symbol R_F stands for *Ratio of Fronts* or *Retention factor* and is universally used to denote the ratio of the distance travelled by the solute from the origin line and the distance travelled by the solvent from the origin line.

$$R_F = \frac{\text{Distance travelled by the solute from the origin line}}{\text{Distance travelled by the solvent from the origin line}}$$

For example in Fig. 2·16 centre of the spot B for a particular substance is at a distance x from the origin A (the point of application of the substance) whereas solvent front has moved through a distance y from the origin.

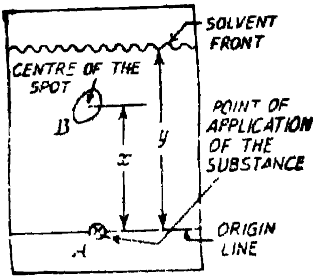

Fig. 2·16.

Hence in this case

$$R_F = \frac{x}{y}$$

R_F of a substance depends on :

(*i*) Nature of solvent used,
(*ii*) Quality of paper,
(*iii*) Nature of the substance,
(*iv*) Temperature.

Instead of a single substance if we use mixture of two substances A and B, they will rise through different distances (say x cm and y cm respectively) whereas the solvent rises through a distance z cm. From this data

$$R_F \text{ for } A = x/z$$

$$R_F \text{ for } B = y/z$$

Ratio between their R_F values

$$= \frac{x}{z} : \frac{y}{z} :: x : y$$

Thus we can compare the R_F values of the components of a mixture.

Analysis of mixtures of amino-acids may be carried out with the help of paper chromatography. Mark six points on a filter paper. Aqueous solution of the mixture is put at one point and standard solutions of five different amino-acids suspected to be present are put at five remaining points. The filter paper is held vertical and its lower end dipped in a solvent which may be *n*-butanol-ethanol-water mixture or *n*-butanol-acetic acid-water mixture. When the solvent layer travels sufficient height, filter paper is removed and dried. It is next sprayed with a dilute solution of ninhydrin in *n*-butanol or ethanol when coloured spots are seen.

If the mixture gives three different spots at different heights, it is a mixture of three different amino-acids. Comparison of the R_F values of these spots with the R_F values of spots given by five known amino-acids, we can deduce the identity of the amino-acids. Colour of each spot is proportional to the amount of amino-acid present. The colours produced by mixture spots are compared with those of known acids photometrically and the quantities of the amino-acids present are thus quantitatively estimated.

Analysis of a mixture of sugars is carried out in a similar manner, using the same solvent system. However, the filter paper in this case is sprayed with aniline hydrogen phthalate.

(c) **Gas chromatography**. In this the stationary phase is either a solid (GSC) or a high boiling liquid deposited on a suitable support (GLC), such as molten vacuum grease or silicone oil, impregnated on a powder support and packed in a column. The liquid must be non-volatile at the temperature used. Out of the two GLC is more common. The moving phase is a carrier gas, such as nitrogen, helium or argon which does not react with the sample. The whole column is placed in a thermostat.

The sample may be gaseous, liquid, solution of a solid in a suitable solvent (like hexane, benzene or acetone) or solid itself provided it is appreciably volatile at the column temperature. The sample is introduced in the column with the help of a syringe (if vapour or liquid) and the carrier gas passed through. On account of the temperature at which the instrument is maintained, the sample vaporises readily. The carrier gas sweeps the vapour of the sample into the coil filled with stationary phase.

The carrier gas is trying to sweep out the constituents of the sample through the other end of the column. At the same time, high boiling liquid in the column is trying to retain them. Partitioning of every constituent of the material vapour thus occurs between the carrier gas and the liquid in the column. This distribution differs from constituent to constituent. The least soluble constituent comes out first while the most soluble constituent comes out the last.

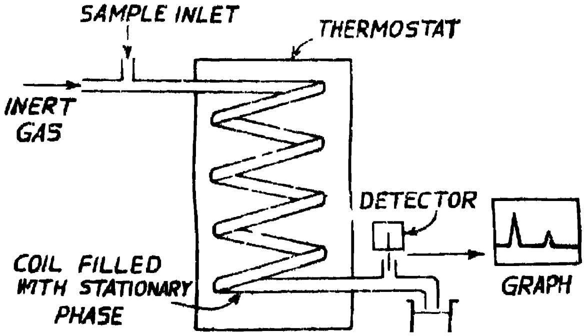

Fig. 2·17—Gas chromatography.

Thus the components of the mixture are separated in the form of their vapours. The emerging gas is passed through a detector whose electrical response depends on the concentration of the sample in the gas stream. The detector is provided with an automatic chart recorder. The trace produced by the pen recorder is known as a chromatogram. A typical gas chromatogram is shown in Fig. 2·18.

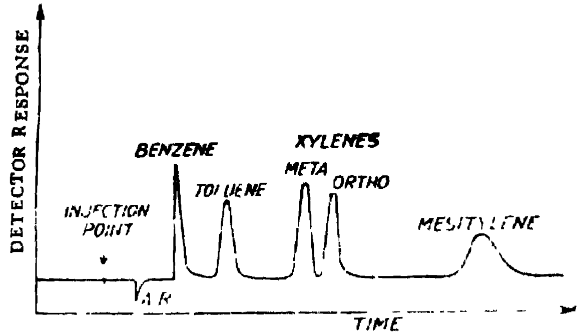

Fig. 2·18—A typical gas chromatogram.

Gas chromatography is used largely as an analytical tool, where it can handle minute quantities (as small as 10^{-9} g) of samples and effect remarkable separations.

(9) **Zone Refining**. Zone refining is the name given to a family of techniques involving the production of a molten zone in a bar or column of solid material and is of particular interest to chemists.

The principle underlying the technique is to take a column of the substance in a tube, which is normally of glass and mounted in the vertical position with an electrical heating loop around the tube (*see* Fig. 2·19). The tube is lowered slowly through the heating loop around the tube which melts the solid in the section of the tube enclosed by the loop. As the tube progresses downwards, the pure solid begins to form from the melt at the base of the molten zone. Most of the impurities remain in the molten zone that is moved upward through the tube. The impurities are thus concentrated in the molten zone and are carried forward to the top of the column. By repeating the process a number of times it *is possible to produce materials of an extremely high degree of purity which it would be difficult to produce by other means. The purest material is generally to be found in the lower part of the tube.*

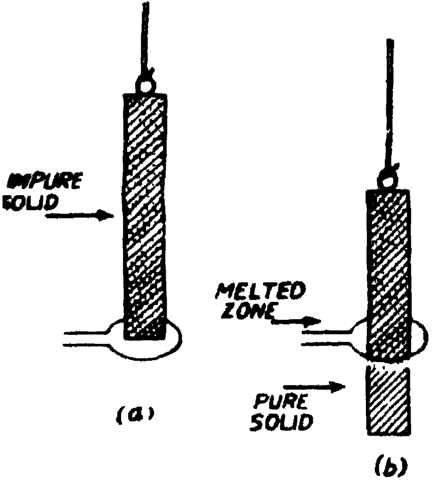

Fig. 2·19—Zone refining.

To achieve a degree of purity comparable to that obtained by zone refining an impossibly large number of recrystallisations would be required. Furthermore, the loss of material by rejection of the mother liquor and due to handling losses would be very considerable. Zone refining does not suffer from these disadvantages. The technique is, however, not a rapid one. Several passages of the heater are required and the molten zone must pass only slowly up the tube at a speed in the region of one inch per hour. However, by using a suitable apparatus the process can be carried out automatically or semi-automatically and the equipment can be left to operate with little or no supervision.

(10) **Chemical Methods.** For purification of organic substances, very often advantage is taken, in practice, of the acidic or basic character of its various components. For example, a mixture of aniline and toluene can be separated by treating it with excess of dilute hydrochloric acid in a separating funnel. Lower aqueous layer of aniline hydrochloride is separated and treated with sodium hydroxide when aniline separates as a colourless oily liquid. Toluene remains behind in the separating funnel.

Apart from this, a substance may frequently be converted into a crystalline derivative by means of a reagent which does not react with the impurities. The solid derivative is recrystallized, if necessary, and decomposed to get pure substance. For example, crude acetone prepared from pyroligneous acid is shaken with a strong solution of sodium bisulphite. The acetone forms a crystalline bisulphite compound which is separated from the impurities. The crystalline compound decomposes when warmed with a solution of sodium carbonate or sodium hydroxide. Acetone, so liberated, is distilled, dried over anhydrous calcium chloride and redistilled.

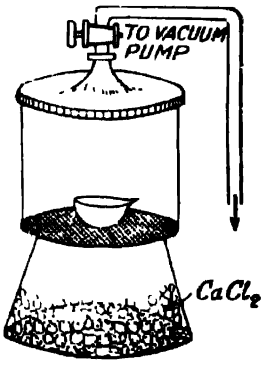

Fig. 2·20—Vacuum desiccator

Methyl alcohol and acetaldehyde are purified in a similar manner by forming their crystalline derivatives.

5. **Drying of Organic Substances.**—An organic compound cannot be regarded as pure even if it contains traces of moisture. In some cases presence of moisture is enough to affect fundamentally the chemical properties of the substance. Organic liquids are generally dried by keeping them in contact with a desiccating agent which does not react chemically with the liquid. Common drying agents generally used are quicklime, fused calcium sulphate or copper sulphate and solid caustic potash. For example, alcohol is dried over quicklime or anhydrous copper sulphate and it cannot be dried over fused calcium chloride as it reacts with it chemically.

Solids, if sufficiently stable, are dried by heating them gently in a steam or air oven. Those substances which decompose on heating are dried at the ordinary temperature in a vacuum desiccator charged with a suitable desiccating agent (Fig. 2·20).

6. **Criteria of Purity.**—It is important to test the purity of an organic compound after purification and proper drying. Usual tests employed to serve as criteria of purity are :

FOR SOLIDS

(*i*) **Microscopic Examination.** In case the organic compound is a crystalline solid, it is examined under a microscope. Homogeneous crystals (with similar geometrical shape), if seen under the microscope, indicate it to be roughly pure. It is not a sure test as mixtures of isomorphous substances also appear homogeneous when seen under a microscope.

(*ii*) **Melting Point.** The criterion of purity of a solid organic substance is a sharp melting point which remains unchanged on recrystallization. Presence of impurities lowers the melting point of a substance.

The melting point is determined by means of some such apparatus as that shown in the diagram (Fig. 2·21). Finely powdered substance is taken in a capillary tube sealed at the lower end, wetted by the liquid of the bath and attached to thermometer (viscosity of the acid and surface tension keep the capillary tube clinging to the thermometer). The thermometer is then lowered into a Thiele tube containing conc. sulphuric acid. The Thiele tube is slowly heated. The exact temperature at which the opaque solid becomes transparent gives the melting point. The solid is purified again and its melting point re-determined. If the two melting points are sharp and concordant, the substance is pure.

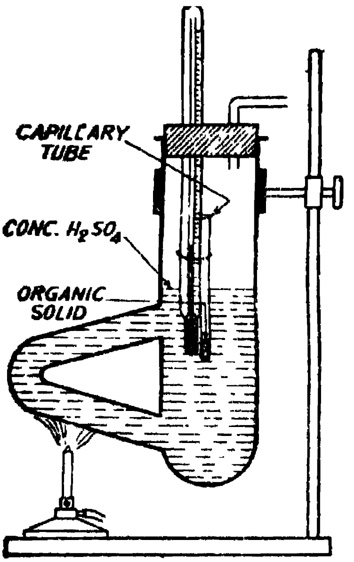

Fig. 2·21—Determination of melting point by Thiele's method.

Electrically heated Melting point apparatus. It consists of an aluminium block in which three capillary melting point tubes and a thermometer can be inserted. A lamp mounted in front of the apparatus provides uniform and shadowless illumination of the sample tubes which are viewed through a lens. The apertures in the block are screened by sheets of glass to exclude droughts and to ensure uniform temperature.

One heater is regulated by a built-in rotary rheostat which gives an accurate adjustment of the rate of increase of temperature as the melting point is approached. The other heater for boosting the heating rate is controlled by switch. A second switch controls the lamp and the power input to the apparatus. Ventilation is provided to enable the block to be cooled quickly between determinations.

Main features of this apparatus are fine temperature control and accurate results obtained quickly.

(*iii*) **Mixed Melting Point** The purified sample is mixed with a little of the pure substance and the melting point of the mixture determined. If the mixture melts at the melting point of the pure substance, the sample is pure otherwise it needs further purification.

FOR LIQUIDS

(*i*) **Boiling Point** The criterion of the purity of an organic liquid is sharp and concordant *boiling point* The liquid, if available in sufficient quantity, is boiled in a distillation flask and the constant temperature at which the liquid distils over gives its boiling point

If the liquid is available in small quantity, it is taken in a small fusion tube attached to thermometer with a rubber band A small capillary tube, with its upper end sealed, is dipped in the liquid and the thermometer is lowered into a Thiele tube containing conc sulphuric acid (Fig 2.22) The Thiele tube is slowly heated and the temperature at which a brisk evolution of bubbles occurs at the lower end of the capillary tube gives its boiling point The value is compared with the one given in the table of physical constants For an unknown liquid sharp and concordant value implies that it has been obtained in a pure state

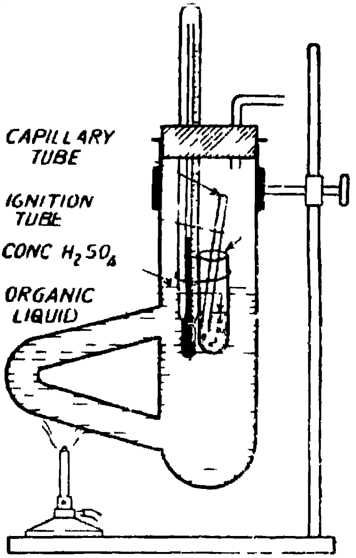

Fig 2.22 Determination of boiling point by Thiele's method

(*ii*) **Specific Gravity and Refractive Index** In addition to boiling point, constant values of specific gravity and refractive index of a liquid also serve as criteria of purity

QUESTIONS

Essay Type

1 Write an account of the various methods by which organic compounds are purified What are the criteria of purity for organic liquids and solids ?

2 With the help of a sketch describe the extraction of oil from seeds using Soxhlet apparatus (*Bangalore B Sc 1969*)

3 (*a*) Name the process of purifying an organic liquid which decomposes on heating to its boiling point Illustrate it with a diagram

(*b*) Write a short account of the method of purification by chromatography (*Delhi B Sc Hons 1973*)

4 What use is made of the following in the Organic Chemistry ?

(*a*) Mixed melting point (*b*) Fractional crystallization.

(*c*) Distillation under reduced pressure. (*Agra B Sc. 1968*)

5 Describe briefly how you would separate a mixture of amino-acids chromatographically State the principle involved in the separation What is R_F value ? (*Delhi B Sc. Hons I. 1976*)

6. Explain and illustrate any two of the following :
(*a*) Vacuum distillation, (*b*) Steam distillation, and (*c*) Sublimation.
(*Delhi B.Sc.Hons. Sub. 1976*)

7. How would you proceed to test the purity of an organic liquid? Describe a practical method for finding out the boiling point of a pure organic liquid which is available in a small quantity
(*Delhi B.Sc. Hons. Sub. I, 1976 Supp.*)

8. Give two physical methods to test the purity of an organic compound.
(*Delhi B.Sc. 1976 Supp.*)

9. What is steam distillation? What is its advantage in purifying organic compounds?
(*Calicut B.Sc. 1978*)

10. In an organic reaction two volatile organic liquids A and B with boiling point 333·5K and 340K were formed. What method would you adopt to get them in pure state? Discuss the principle of this method.
(*Delhi B.Sc. Hons. Sub. 1978*)

11. How will you purify the mixture of liquids by fractional distillation? How will you ascertain that the sample obtained is pure?
(*Delhi B.Sc. Hons 1978*)

Short Answer Type :

1. Name the criteria of purity of organic compounds.
2. Name the processes used for purification of—
   (*i*) an organic liquid which decomposes on heating to its boiling point
   (*ii*) a solid mixed with a soluble impurity.
3. When is chromatographic technique used?
4. Name different types of chromatographic techniques.
5. What is R_f value?
6. What is the principle underlying steam distillation?
7. What is a chromatogram?
8. What is the principle underlying zone refining?
9. What is the principle underlying mixed melting point determination?
10. What is the use of mixed melting point in identification of organic compounds?
(*Delhi B.Sc. Hons. 1976*)

3

Qualitative Analysis (Detection of Elements)

1. **Molecular Diagnosis.**—For the investigation and characterisation of an organic compound after it has been obtained in a pure state, a complete molecular diagnosis is necessary. This involves the following steps :

(*a*) *Detection of Elements*, *i.e.*, the determination of the qualitative elementary composition of the substance. This resolves itself into a process of testing for the elements present in organic compounds.

(*b*) *Estimation of Elements*, *i.e.*, the determination of the quantitative elementary composition or percentage composition of the substance.

(*c*) *Calculation of the Empirical Formula.* The percentage composition found above leads to the calculation of the Empirical Formula of the substance.

(*d*) *The determination of Molecular Weight, leading to the calculation of the Molecular Formula.*

(*e*) *Detection of Functional groups.*

(*f*) *Estimation of Functional groups.*

(*g*) *The determination of the Molecular Structure.* Elucidation of the molecluar constitution necessitates a close study of the chemical relationships of the substances. The formula depicting the molecular structure of the substance is called **structural formula** and is often confirmed by synthesis. It summarizes the chemical behaviour of the substance.

2. **Detection of Carbon and Hydrogen.**—Presence of carbon in a compound may be assumed if it is definitely known to be an organic compound whilst hydrogen is rarely absent. Many organic compounds either burn with a sooty flame or char when strongly heated. Detection of Carbon and hydrogen in a given substance is, however, carried out by oxidising the substance with copper oxide at high temperature.

A mixture of organic compound and dry copper oxide (black) is heated in a dry test tube fitted with a delivery tube provided with a bulb. The other end of the delivery tube is dipping under lime water (Fig. 3·1).

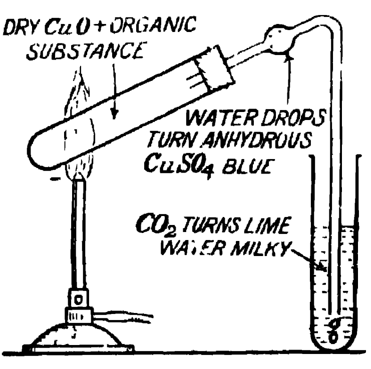
DRY CuO+ORGANIC SUBSTANCE
WATER DROPS TURN ANHYDROUS $CuSO_4$ BLUE
CO_2 TURNS LIME WATER MILKY

Fig. 3·1—Detection of carbon and hydrogen.

Carbon and hydrogen of the organic compound, if present, are oxidised to carbon dioxide and water respectively. Carbon dioxide turns lime water milky whereas water condenses in the bulb and can be tested with the help of anhydrous (*white*) copper sulphate which turns blue. Different reactions can be represented as :

$$2CuO + C \rightarrow 2Cu + CO_2$$
$$CuO + 2H \rightarrow Cu + H_2O$$

Cupric oxide is a hygroscopic substance. It should, therefore, be carefully ignited before use. Apparatus used should also be absolutely dry and free from moisture.

If the substance happens to be a volatile liquid or a gas, the experiment has to be modified. The vapours of the volatile liquid or the gas are passed through wire-form copper oxide heated in a hard glass tube and the outcoming gases are tested for carbon dioxide and water vapour as given above.

3. Detection of Nitrogen.—The following tests are performed to detect the presence of nitrogen in an organic compound.

(*a*) **Action of Heat.** Organic compounds containing nitrogen generally give a burning hair smell when heated strongly. A negative result in this test is, however, not a proof of the absence of nitrogen.

(*b*) **Soda-lime Test.** Many nitrogenous organic compounds yield ammonia when they are heated with soda-lime.* Liberation of ammonia gas on heating the organic compound with soda-lime confirms the presence of nitrogen in the organic compound.

$$\underset{\text{Acetamide}}{CH_3CONH_2} + \underset{\text{Soda-lime}}{NaOH} \rightarrow \underset{\text{Sod. acetate}}{CH_3COONa} + \underset{\text{Ammonia}}{NH_3}$$

Of course, absence of ammonia gas does not confirm absence of nitrogen as all nitrogenous compounds do not respond to this test, *e.g.*, nitro- and diazo- compounds.

Expt. 1. Heat some urea with soda-lime in a hard glass test tube and test the ammonia gas evolved.

(*c*) **Lassaigne's Test.** A small piece of freshly cut sodium metal (pea size) is melted in a small fusion tube and fused with the organic compound. The red-hot tube is broken by immersion in cold distilled water in a dish. The glass pieces are boiled in water to extract the fused mass and filtered. Nitrogen, if present, combines with sodium and carbon of the organic compound to form sodium cyanide. The rest of the process, therefore, consists in testing the solution, so obtained, for the presence of a cyanide.

$$\underset{\substack{\text{Sodium}\\ \text{metal}}}{Na} + \underset{\substack{\text{From organic}\\ \text{compound}}}{C + N} \rightarrow \underset{\substack{\text{Sodium}\\ \text{cyanide}}}{NaCN}$$

The solution is made alkaline with caustic soda if not so already. It is then treated with a fresh solution of ferrous sulphate, boiled and cooled. The solution is acidified with dilute sulphuric acid. Appearance of a green or Prussian blue colour confirms the presence of nitrogen in the organic compound.

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* Soda-lime is lime which has been slaked with caustic soda solution.

Chemistry of the Reaction. Sodium cyanide reacts with ferrous sulphate to form sodium ferrocyanide, $Na_4Fe(CN)_6$.

$$FeSO_4 + 2NaCN \rightarrow Fe(CN)_2 + Na_2SO_4$$

$$\underset{\text{Ferrous cyanide}}{Fe(CN)_2} + 4NaCN \rightarrow \underset{\text{Sod. ferrocyanide}}{Na_4[Fe(CN)_6]}$$

Sodium ferrocyanide reacts with ferric ions produced by oxidation of Fe^{2+} by air in presence of OH^- to give a precipitate of Prussian blue, $NaFe[Fe(CN)_6]$. Sulphuric acid is added to dissolve the bluish green ferrous hydroxide which might otherwise mask the Prussian blue precipitate. Ferrous hydroxide is precipitated by the action of caustic soda on ferrous sulphate.

$$\underset{\substack{\text{Sodium}\\\text{ferrocyanide}}}{Na_4[Fe(CN)_6]} + \underset{\substack{\text{Ferric}\\\text{ion}}}{Fe^{3+}} \rightarrow \underset{\substack{\text{Sod. ferric ferrocyanide}\\\text{(Prussian blue)}}}{NaFe[Fe(CN)_6]} + 3Na^+$$

N.B. (1) Sometimes when the amount of nitrogen present is small, the Prussian blue is present in colloidal form and the solution is green.

(2) If sulphur be present along with nitrogen, metallic sodium combines with C, N and S of the organic compound to form sodium sulphocyanide which gives a blood-red colour due to the formation of ferric sulphocyanide with addition of ferric chloride.

$$Na + C + N + S \longrightarrow \underset{\text{Sod. sulphocyanide}}{NaCNS}$$

$$CNS^- + Fe^{3+} \longrightarrow \underset{\textit{(Blood red in colour)}}{[Fe(CNS)]^{2+}}$$

(*d*) **Evolution of Nitrogen.** Lassaigne's test fails in case of substances like diazo compounds which lose nitrogen at moderate temperatures. In such cases the substance is heated with copper oxide and the gases evolved are tested for nitrogen.

4. **Detection of Halogens.**—An organic compound is tested for the presence of halogens as follows :

(*a*) **Beilstein's Test.** A copper wire is cleaned and heated in a flame till it imparts no colour to it. Now a small amount of organic compound is taken on the copper wire and heated in the flame. A green colour, if imparted to the flame, is due to the formation of a volatile copper halide and proves the presence of a halogen. The test is not very satisfactory as some compounds not containing halogens also respond to it, *e.g.*, urea.

(*b*) **Lassaigne's Test.** The organic compound is fused with sodium metal as given under detection of nitrogen. The filtrate contains a sodium halide if the original organic compound contained a halogen. Sodium cyanide may also be present if nitrogen were present in the original compound. The filtrate is boiled with concentrated nitric acid to get rid of any sodium cyanide which would otherwise give a white precipitate of silver cyanide with silver nitrate solution and we will confuse it for silver chloride.

Friedrich K. Beilstein (1836-1906)—Russian chemist and compiler of the monumental "Hand Book of Organic Chemistry"—A book in over fifty volumes. Beilstein's test for detection of halogens is due to him.

$$\mathrm{Na} + \underset{\text{Halogen}}{\mathrm{X}} \rightarrow \underset{\text{Sod halide}}{\mathrm{NaX}}$$

$$\mathrm{Na} + \underset{\text{From org compd}}{\mathrm{C + N}} \rightarrow \underset{\text{Sod cyanide}}{\mathrm{NaCN}}$$

$$\mathrm{NaCN} + \mathrm{HNO_3} \rightarrow \mathrm{NaNO_3} + \mathrm{HCN}\uparrow$$

The solution is cooled and treated with silver nitrate solution. A precipitate proves the presence of halogen—the colour indicates its nature, *viz.*, white—chlorine, straw-yellow—bromine and yellow—iodine.

$$\underset{\text{Sodium halide}}{\mathrm{NaX}} + \underset{\text{Silver nitrate}}{\mathrm{AgNO_3}} \rightarrow \underset{\substack{\text{Silver halide}\\ (\textit{precipitate})}}{\mathrm{AgX}} + \mathrm{NaNO_3}$$

Quicklime may be used in place of sodium. This avoids the necessity of decomposing sodium cyanide. The residue is extracted with water and filtrate is tested with silver nitrate solution as given above.

Sodium metal used in Lassaigne's test can be conveniently replaced by sodium carbonate and sugar mixture or sodium carbonate and zinc dust, or magnesium powder and sodium carbonate.

5. **Detection of Sulphur.**—Sulphur may be detected in an organic compound by either of the following tests :

(*a*) **Lassaigne's Test.** The organic compound is fused with sodium (*see* under nitrogen) and the filtrate contains sodium sulphide, if sulphur were present in the organic compound.

$$2\mathrm{Na} + \mathrm{S} \rightarrow \mathrm{Na_2S}$$

Presence of sodium sulphide in the filtrate can be confirmed as follows :

(*i*) Treat a test portion with sodium nitroprusside solution, a purple colour is obtained.

$$\mathrm{Na_2S} + \underset{\text{Sod nitroprusside}}{\mathrm{Na_2[Fe(CN)_5NO]}} \longrightarrow \underset{\text{Purple coloured complex}}{\mathrm{Na_4[(FeCN)_5NOS]}}$$

(*ii*) To another test portion add lead acetate solution, a black precipitate of lead sulphide is produced.

$$\mathrm{Na_2S} + \underset{\text{Lead acetate}}{\mathrm{(CH_3COO)_2Pb}} \rightarrow \underset{\text{Black ppt}}{\mathrm{PbS}} + 2\mathrm{CH_3COONa}$$

(*iii*) A drop of the filtrate if taken on a silver coin moistened with hydrochloric acid produces a black stain.

(*b*) **Oxidation Test.** The organic compound is fused with fusion mixture (a mixture of sodium carbonate and potassium nitrate) when sulphur, if present, is oxidised to sodium or potassium sulphate.

$$\mathrm{Na_2CO_3} + \mathrm{S} + 3\mathrm{O} \rightarrow \mathrm{Na_2SO_4} + \mathrm{CO_2}$$

The fused mass is dissolved in water, acidified with hydrochloric acid and tested for the presence of a sulphate radical with barium chloride solution. A white precipitate with barium chloride indicates the presence of sulphur in the organic compound.

For *volatile substances*, which do not respond to the above test as they evaporate before they can fuse, proceed as under :

Heat the organic compound with fuming nitric acid in a sealed tube. Sulphur, if present, is oxidised to sulphuric acid which gives a white precipitate with barium chloride, insoluble in all acids.

6. **Detection of Phosphorus.**—The organic compound is fused with the fusion mixture when phosphorus, if present, is oxidised to a phosphate. The fused mass is extracted with water and heated with concentrated nitric acid and ammonium molybdate. A yellow precipitate or coloration on heating and cooling indicates the presence of phosphorus.

Oxidation of phosphorus to phosphoric acid may also be brought about by heating with fuming nitric acid, as in the case of volatile sulphur compounds above.

7. **Detection of Metals.**—A little of the organic compound is placed on a platinum foil or in a china dish and heated strongly. An incombustible residue indicates the presence of metals. It is dissolved in an acid and analysed in the way usually employed for inorganic substances.

QUESTIONS

Essay Type :

1 How do you detect carbon and hydrogen in an organic compound ?
(Calicut B Sc. 1978)

2. How can you identify halogens and nitrogen when they occur together in an organic compound ? Explain the chemical reactions involved.

3. Describe briefly the tests used to detect the following elements in organic compounds :

(*a*) Carbon and hydrogen. (*b*) Nitrogen. (*c*) Phosphorus.

(*d*) Sulphur. (*e*) Halogens.

Describe the chemistry of reaction in each case
(Punjab B Sc Part I, 1979)

4 Describe Lassaigne's test to detect nitrogen in an organic compound containing halogen. *(Delhi B Sc I, 1976)*

5 Write a short note on Lassaigne's test.
(Punjab T.D C. Part I, 1979 , Delhi B Sc Hons. Sub 1976)

Short Answer Type :

1. While testing for halogens, why is sodium extract in Lassaigne's test boiled with nitric acid ?

2. Soda-lime test for detection of nitrogen is misleading. Why ?

3. Why is dry copper oxide used in the detection of hydrogen ?

4. Write equation for the reactions involved in the Lassaigne's test used for the detection of

(*i*) nitrogen, and

(*ii*) sulphur.

5. Is Beilstein's test a satisfactory test for detection of halogens ? Give reasons.

4

Quantitative Analysis (Estimation of Elements)

1. Introduction.—After detection of elements the next step in the molecular diagnosis of an organic compound is its *quantitative analysis*. This consists in estimation of various elements present, *i.e.*, finding the percentage composition of the substance by weight. Different methods employed for the quantitative determination of the proportions of the elements in an organic compound are given below.

2. Estimation of Carbon and Hydrogen (*Liebig's combustion method*).—Estimation of carbon and hydrogen is invariably carried out simultaneously. The method used is only an extension of the method described on page 125 for detection of these elements.

PRINCIPLE

If an organic compound is strongly heated with dry cupric oxide, carbon present is oxidised to carbon dioxide while hydrogen present is oxidised to water vapour. The apparatus is so designed that the carbon dioxide and water formed can be collected and weighed separately. Knowing the weights of these products, percentage of carbon and hydrogen can be calculated.

APPARATUS USED

The apparatus used for the purpose consists of the following units :

(*i*) **Oxygen Supply.** Oxygen is passed through tubes containing pumice stone soaked in concentrated sulphuric acid and KOH to remove moisture and CO_2. Dry oxygen free from CO_2 thus obtained is supplied to the combustion tube.

(*ii*) **Combustion Tube.** It is a hard glass tube *AB* open at both ends, about 12-15 mm in internal diameter and about 90 cm in length. It is packed as shown in the diagram (Fig. 4·1). A layer of wire-form copper oxide held between two asbestos pads is placed in position and roll of oxidised copper spiral is placed on its right. The end *B* is next closed by a rubber stopper through which a delivery tube passes. On the left side of the wire-form copper oxide is placed a porcelain boat and an oxidised copper spiral both attached to each other and attached to the cork on the left. Thus by pulling

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Liebig Justus, Baron von (1803-73)—German chemist, a devoted and gifted teacher whose laboratory was for many years the Mecca of chemists from all Europe and beyond. The combustion method for the estimation of carbon and hydrogen is due to him.

out the cork on the left both oxidized copper spiral and porcelain boat are taken out. The hard glass tube is heated in a combustion furnace.

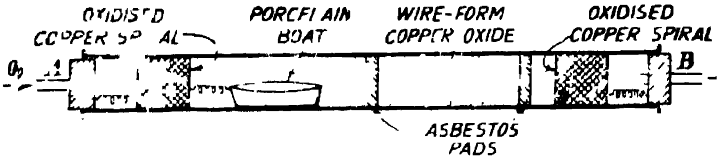

Fig 4 1—Combustion tube.

(iii) **Combustion Furnace** The furnace used in the estimation of elements by combustion method consists of a semi-cylindrical iron tray about 80 cm long and lined with asbestos. The iron tube placed in the furnace is heated by a row of gas burners fitted in the [illegible] and is kept covered at the top by fire-clay tiles.

(iv) **Absorption Apparatus** The products of combustion are carbon dioxide and water vapour. The apparatus used for absorption of these consists of

(a) A weighed calcium chloride tube containing granulated (not fused) and sieved calcium chloride* to absorb water vapour and

(b) Potash bulbs containing 50 per cent caustic potash solution to absorb carbon dioxide

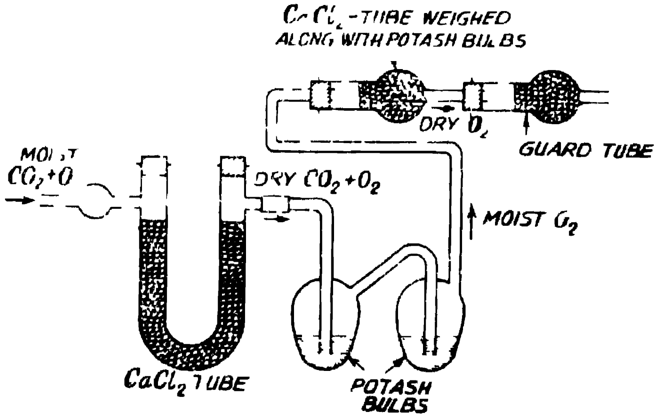

Fig 4 2—Absorption apparatus.

A small calcium chloride tube is weighed along with the potash bulbs to absorb any moisture that the bubbling gases are likely to take away with them from the potash bulbs.

In a modern absorption apparatus the potash bulbs and the calcium chloride tube weighed along with the potash bulbs are replaced by a weighed U-tube filled with saphnolite (a resin). This absorbs carbon dioxide and changes from red to white. The increase in weight of the saphnolite tube gives the weight of carbon dioxide. Thus a modern absorption apparatus consists of a calcium chloride tube to absorb water vapour, a saphnolite tube to absorb carbon dioxide and a guard tube to ward off the atmospheric moisture.

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* The calcium chloride used must be free from any lime or basic chloride present by treating with carbon dioxide

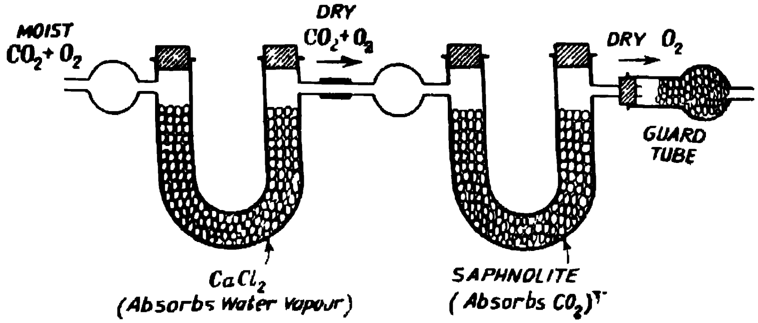


Fig 4·3—Modern absorption apparatus

PROCEDURE

(i) The combustion tube is placed in the furnace and connected at the end *A* to a Drechsel bottle containing concentrated sulphuric acid, to gauge the rate of flow of gas. At the end *B* it is connected to an unweighed calcium chloride tube (*guard tube*) to prevent moisture from air diffusing back into the tube.

(ii) It is then heated in a current of dry oxygen for about half an hour. This drives off any moisture or carbon dioxide from the tube and ensures complete oxidation of the copper spiral and copper oxide.

(iii) Next the burners heating the left half of the tube are put off and the tube is cooled. The porcelain boat and the copper

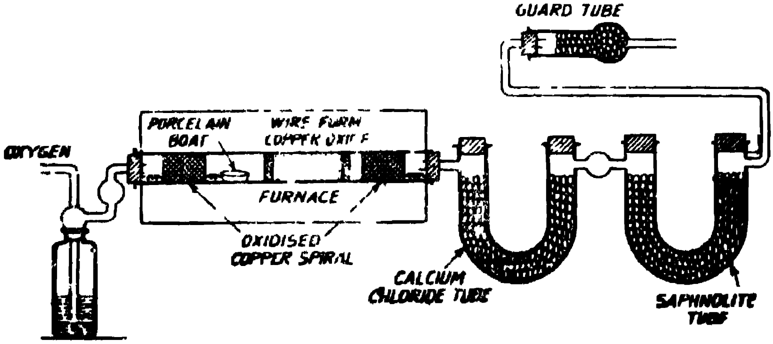


Fig. 4·4—Estimation of carbon and hydrogen.

spiral are taken out momentarily. About 0·2 gram of the carefully dried organic compound is weighed out in the porcelain boat as such or obtained in a bulb (*for volatile liquids*) and the boat is replaced.

(*iv*) Now the guard tube is detached from the end *B* and the absorption apparatus connected as shown (Fig. 4·4). A guard tube attached to the absorption apparatus serves to prevent any atmospheric moisture from coming in.

(*v*) The burners are next lighted first under the oxidised copper spiral and then under the boat. Heating is continued for about three hours in a current of dry oxygen.

(*vi*) When the reaction is over, the absorption apparatus is disconnected and weighed.

Calculation. Increase in weight of calcium chloride tube gives the weight of water produced ($=x$ g, say) and increase in weight of saphnolite tube gives the weight of carbon dioxide ($=y$ g, say) produced by the combustion of organic compound (W g, say). From these weights the percentage of carbon and hydrogen is calculated as follows :

Since 44 parts by weight of carbon dioxide (CO_2) contain 12 parts by weight of carbon, the amount of carbon present in y g of

$$\text{carbon dioxide} = y \times \frac{12}{44} \text{ g.}$$

This much carbon is present in W g of the substance.

$$\text{Hence percentage of carbon in the compound} = y \times \frac{12}{44} \times \frac{100}{W}$$

Similarly, as 18 parts by weight of water (H_2O) contain 2 parts by weight of hydrogen the amount of hydrogen present in x g of

$$\text{water} = x \times \frac{2}{18} \text{ g.}$$

This much hydrogen is present in W g of the substance.

Hence percentage of hydrogen in the organic compound

$$= x \times \frac{2}{18} \times \frac{100}{W}$$

$$\text{Hence percentage of C} = \text{Wt of } CO_2 \times \frac{12}{44} \times \frac{100}{\text{Wt of substance}}$$

$$\text{and percentage of H} = \text{Wt of } H_2O \times \frac{2}{18} \times \frac{100}{\text{Wt of substance}}$$

Precautions. (*i*) Combustion tube and its contents should be free from moisture and carbon dioxide.

(*ii*) Flow of air through the combustion tube should be properly regulated.

NECESSARY MODIFICATIONS

(*a*) **If the substance contains nitrogen,** it would be oxidised to oxides of nitrogen which are absorbed in the potash bulbs. A bright copper gauze spiral is placed near the exit. This reduces the oxides of nitrogen to nitrogen gas which escapes unabsorbed.

(*b*) **If the substance contains halogens,** volatile copper halides are produced and absorbed in one part or the other of the absorption apparatus. A roll of silver is placed near the exit. This helps to decompose these copper halides and form non-volatile silver halides.

(*c*) **In case the substance contains halogens and sulphur,** a layer of lead chromate is placed near the exit. This is an oxidising agent and forms non-volatile lead halides and reacts with sulphur dioxide formed during combustion to form lead sulphate (*non-volatile*).

NECESSARY MODIFICATIONS

(*a*) **If the substance contains nitrogen or sulphur**, these will be oxidised to NO_2 and $SO_2 + SO_3$ and will be absorbed in potash bulbs. The gases are, therefore, first passed over heated lead dioxide and then admitted into the absorption apparatus. Lead dioxide absorbs NO_2 forming lead nitrate and SO_2 or SO_3 forming lead sulphate. Lead sulphate can be separated and weighed. From this we can calculate the percentage of sulphur. Carbon, hydrogen and sulphur can thus be estimated in one operation.

(*b*) **If the substance contains both nitrogen and halogens**, the products of combustion are passed over a heated silver spiral placed in a porcelain boat and then admitted into the absorption apparatus. The oxides of nitrogen are reduced to nitrogen gas which escapes. The halogen gives silver halide. Percentage of halogen can be calculated from the increase in weight of silver spiral. Carbon, hydrogen and the halogen can thus be estimated in one operation.

3. **Estimation of Oxygen.**—Until recently there was no satisfactory method for direct estimation of oxygen in an organic compound. After finding the percentage of various elements present other than oxygen, percentage of oxygen was calculated by difference as illustrated in the following example :

Example 1. *0·20 g of an organic compound containing carbon, ydrogen and oxygen yielded on combustion 0·147 g carbon dioxide and ·12 g water. Calculate the percentage composition of the substance.*

Weight of organic compound taken $= 0{\cdot}20$ g.

,, ,, carbon dioxide produced $= 0{\cdot}147$ g.

,, ,, water produced $= 0{\cdot}12$ g.

$$\text{Percentage of carbon} = \text{Wt of } CO_2 \times \frac{12}{44} \times \frac{100}{\text{Wt of substance}}$$

$$= 0{\cdot}147 \times \frac{12}{44} \times \frac{100}{0{\cdot}20} = \mathbf{20{\cdot}04}$$

$$\text{Percentage of hydrogen} = \text{Wt of } H_2O \times \frac{2}{18} \times \frac{100}{\text{Wt of substance}}$$

$$= 0{\cdot}12 \times \frac{2}{18} \times \frac{100}{0{\cdot}20} = \mathbf{6{\cdot}66}$$

Percentage of oxygen (*by difference*) $= 100 - (20{\cdot}04 + 6{\cdot}66) = \mathbf{73{\cdot}30}$.

There is now, however, a **direct semi-micro method for estimation of oxygen**. The organic compound is subjected to pyrolysis in a stream of nitrogen. The products are passed over heated carbon at 1393K when all the oxygen in products is converted into carbon monoxide. The carbon monoxide is then passed over iodine pentoxide, and the iodine liberated is estimated titrimetrically.

4. **Estimation of Nitrogen.**—Nitrogen present in an organic compound may be estimated in several ways but only three methods are commonly employed. These are :

(*i*) Dumas' method, (*ii*) Kjeldahl's method, and

(*iii*) Ter Meulen's method.

5. **Dumas' Method.**—This method, which is applicable to all organic compounds containing nitrogen, is also a combustion method like one used for the estimation of carbon and hydrogen.

PRINCIPLE

The method is based upon the fact that when an organic compound is heated strongly with copper oxide and the products of combustion passed over a bright copper spiral, carbon, hydrogen and sulphur are oxidised to carbon dioxide, water and sulphur dioxide, respectively. These can be absorbed in caustic potash solution. Nitrogen, if oxidised, will again be reduced to nitrogen by reduced copper spiral. From the volume of nitrogen collected over caustic potash, percentage of nitrogen can be calculated.

APPARATUS USED

The apparatus used for the purpose as shown in Fig. 4·5 consists of :

(*i*) **Carbon dioxide generator.** The current of oxygen is replaced in nitrogen estimation by a current of carbon dioxide which may contain water vapour but it must be free from nitrogen. The carbon dioxide generator often consists of a hard glass tube containing magnesite ($MgCO_3$) or a Kipp's apparatus containing marble and dilute hydrochloric acid.

$$\underset{\text{Magnesite}}{MgCO_3} \xrightarrow{\text{Heat}} MgO+CO_2$$

$$\underset{\text{Marble}}{CaCO_3}+2HCl \longrightarrow CaCl_2+CO_2+H_2O$$

(*ii*) **Combustion Tube.** It is a hard glass tube open at both ends, about 12-15 mm in internal diameter and about 90 cm in length. It can be placed in an iron tube and heated in a combustion furnace. The combustion tube is packed as shown in Fig. 4·5.

Near the entrance on the left is an oxidised copper roll. Next is a layer of fine copper oxide mixed with a known weight of the organic compound held in position between two wire-gauze plugs. This is followed by a layer of wire-form copper oxide similarly placed between two wire-gauze plugs. Near the exit on the right is placed a bright copper spiral.

(*iii*) **Combustion Furnace.** It consists of a semi-cylindrical iron tray about 80 cm long and lined with asbestos. The iron tube placed in the furnace is heated by a row of gas burners fitted in the iron tray and is kept covered at the top by the fire-clay tiles.

Dumas, Jean Baptiste Andre (1800-84), French chemist, conducted important researches on organic compounds. The combustion method for the estimation of nitrogen is due to him.

(*iv*) **Schiff's Nitrometer.** It is a graduated tube filled with caustic potash solution and provided with a funnel and a tap at its upper end and two side tubes near the lower end. One of the side tubes is connected with a caustic potash solution reservoir and the other with the combustion tube. A little of mercury at the bottom acts as a seal.

PROCEDURE

The apparatus is fitted as shown, and a known weight of organic substance mixed with fine copper oxide is placed in position. The combustion tube is put in an iron tube and placed in the combustion furnace. A current of carbon dioxide is now passed through the combustion tube. When no more air bubbles collect in the nitrometer, it shows that whole of air has been displaced. Upper tap of the nitrometer is now opened and the reservoir is raised till the caustic potash solution level reaches the tap which is then closed. Burners are now lighted first under the sides and then under the portion containing copper oxide and the substance.

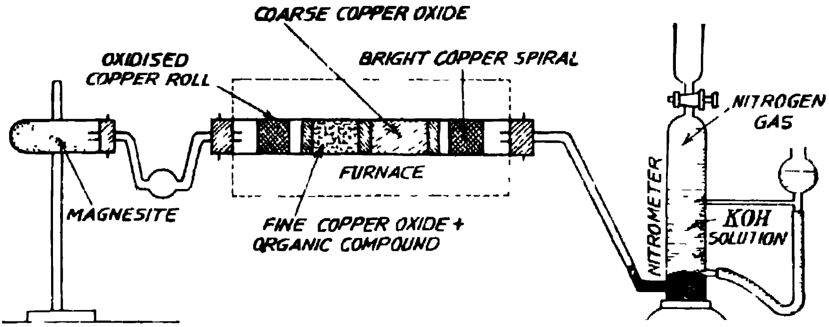


Fig. 4·5—Dumas' method for estimation of nitrogen.

Fine and coarse copper oxide oxidise the organic compound ; oxidised copper spiral oxidises any substance which tends to diffuse that side while bright copper spiral reduces any oxides of nitrogen to gaseous nitrogen.

$$2NO + 2Cu \rightarrow 2CuO + N_2$$

All products of combustion, *e.g.*, carbon dioxide, water vapour and sulphur dioxide, are absorbed by caustic potash except nitrogen gas which collects in the nitrometer.

When the combustion is complete, a rapid stream of carbon dioxide is passed through the combustion tube to sweep away the last traces of nitrogen. The volume of nitrogen is now noted after ***careful levelling (making level of caustic potash solution in the two limbs equal)***. Room temperature and the pressure are also noted.

CALCULATIONS

Knowing the volume, pressure and temperature of nitrogen collected, its volume at NTP is calculated. Then its weight is calculated from the relation that 22·4 litres of nitrogen at NTP weigh 28 g.

$$\text{Percentage of Nitrogen} = \frac{\text{Wt of Nitrogen} \times 100}{\text{Wt of organic substance}}$$

Example 2. *0·2046 g of an organic substance gave 30·4 cm³ of moist nitrogen measured at 288K and 732·7 torr. Calculate the percentage of nitrogen in the substance. [Aq. tension at 288K is 12·7 torr. One litre of nitrogen weighs 1·25 g at NTP.]*

Weight of organic substance taken = 0·2046 g.

Volume of Nitrogen calculated at NTP.

$V_1 = 30{\cdot}4\ \text{cm}^3$ $V_2 = ?$

$P_1 = 732{\cdot}7 - 12{\cdot}7 = 720$ torr. $P_2 = 760$ torr.

$T_1 = 288$ K $T_2 = 273$ K

$$V_2 = \frac{P_1 V_1 T_2}{T_1 P_2} = \frac{720 \times 30{\cdot}4 \times 273}{288 \times 760} = 27{\cdot}30\ \text{cm}^3.$$

$$\text{Wt of 1 cm}^3 \text{ of } N_2 \text{ at NTP} = \frac{1{\cdot}25}{1000} = {\cdot}00125\ \text{g}$$

$$\text{Percentage of Nitrogen} = \text{Wt of Nitrogen} \times \frac{100}{\text{Wt. of sub}}$$

$$= \text{Vol of } N_2 \times \text{Wt of 1 cm}^3 \times \frac{100}{\text{Wt of sub}}$$

$$= 27{\cdot}30 \times {\cdot}00125 \times \frac{100}{0{\cdot}2046} = \mathbf{16{\cdot}68}.$$

6. **Kjeldahl's Method.**—This is a very convenient method generally used for the estimation of nitrogen in agricultural and biological laboratories.

PRINCIPLE

The method depends upon the fact that most of the organic compounds containing nitrogen are quantitatively decomposed to give ammonium sulphate when heated strongly with concentrated sulphuric acid.

PROCEDURE

About 0·5 g of the organic compound is accurately weighed, mixed with about 10 g potassium sulphate, 20 cm³ concentrated sulphuric acid and a drop of mercury or 1 g $CuSO_4$ and heated in a long-necked Kjeldahl's flask (Fig. 4·6). Potassium sulphate is used to raise the boiling point of sulphuric acid whereas mercury or $CuSO_4$ acts as a catalyst. First of all, the contents darken, and then clear up again indicating that the whole of nitrogen has been quantitatively converted into ammonium sulphate.

The contents are now taken in a round-bottom flask and the apparatus is fitted as shown in Fig. 4·7. Strong caustic soda (40%) solution is added from the dropping funnel and the flask is heated. Ammonia liberated is bubbled through a known volume of a standard acid. Some of the standard acid is neutralized while the remaining acid, left over in excess, is back-titrated against a standard alkali.

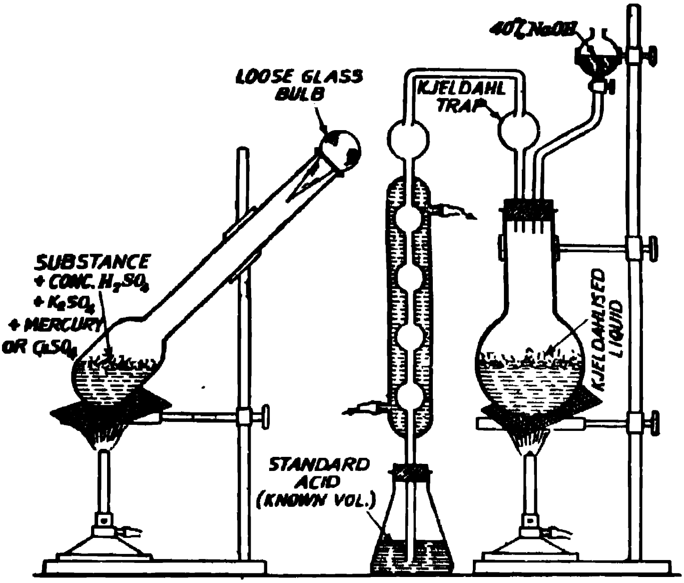

LOOSE GLASS BULB
SUBSTANCE + CONC. H_2SO_4 + K_2SO_4 + MERCURY OR $CuSO_4$
KJELDAHL TRAP
40% NaOH
KJELDAHLISED LIQUID
STANDARD ACID (KNOWN VOL.)

Fig. 4·6—Kjeldahl's flask.

Fig. 4·7—Kjeldahl's method for estimation of nitrogen.

CALCULATIONS

Let V cm³ of N-normal acid be used up for neutralization of ammonia evolved when W g of substance is kjeldahlised.

V cm³ of N-normal acid $\equiv V$ cm³ of N-normal ammonia.

1000 cm³ of normal ammonia contains 17 g of ammonia (NH_3) or 14 g of nitrogen.

∴ Nitrogen present in V cm³ of N-normal ammonia

$$=\frac{14}{1000}\times V\times N=0{\cdot}014\,NV \text{ g.}$$

$$\text{The percentage of nitrogen}=\text{Wt of nitrogen}\times\frac{100}{\text{Wt of sub}}$$

$$=0{\cdot}014\,NV\times\frac{100}{W}=\frac{1{\cdot}4NV}{W}$$

where N=normality of the acid used up

V=volume „ „ „ „ „

and W=Wt of the substance kjeldahlised.

Example 3. *0·1560 g of a nitrogenous substance was kjeldahlised and the ammonia gas evolved from it was absorbed in 60·25 cm³ of N/10-H_2SO_4. After absorption, the excess of the acid required 16·50 cm³ of N/10-NaOH for exact neutralization. Calculate the percentage of nitrogen in the substance.*

Wt. of substance kjeldahlised (W)=0·1560 g

Total N/10-H_2SO_4 taken =60·25 cm³.

Let v cm^3 of this acid be left over unused. This requires 16·5 cm^3 of N/10-NaOH for back-titration.

Writing normality equation, we have

v cm^3 of N/10-H_2SO_4 = 16·5 cm^3 of N/10-NaOH

Applying normality formula, $N_1V_1 = N_2V_2$, we get

$$v \times \frac{1}{10} = 16{\cdot}5 \times \frac{1}{10}$$

or $$v = 16{\cdot}5 \text{ cm}^3.$$

i.e., vol. of the acid left over = 16·5 cm^3.

or vol. of the acid used (V) for neutralization of ammonia

$$= 60{\cdot}25 - 16{\cdot}5 = 43{\cdot}75 \text{ cm}^3 \text{ N/10-}H_2SO_4$$

Now percentage of nitrogen $= \dfrac{1{\cdot}4NV}{W} = \dfrac{1{\cdot}4 \times \frac{1}{10} \times 43{\cdot}75}{0{\cdot}1560} = 39{\cdot}26.$

7. Estimation of Halogens.— Carius Method.

PRINCIPLE

Carius method for estimation of halogens depends on the fact that when a substance containing halogens is heated in a sealed tube with fuming nitric acid in presence of silver nitrate, silver halide is formed. From the amount of silver halide produced the percentage of halogen is calculated.

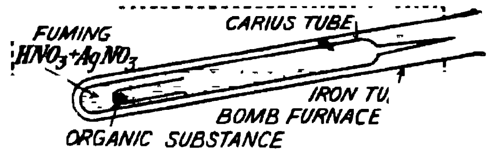


Fig. 4·8—Carius method for estimating halogens.

PROCEDURE

An accurately weighed quantity of organic compound is taken in a narrow 'weighing tube' and lowered into a '*bomb tube*' containing fuming nitric acid and silver nitrate crystals. Upper end of the bomb tube is carefully sealed. It is then enclosed in an iron tube and heated strongly in a bomb furnace (Fig 4·8). Organic compound breaks up and the halogen present gives a precipitate of silver halide.

After about six hours the tube is cooled and its upper end softened when gases present inside under pressure escape. The tube is then broken and the precipitate of silver halide washed, dried and weighed.

CALCULATIONS

One gram molecular weight of silver chloride, AgCl (108+35·5 =143·5 g) contains 35·5 g of chlorine.

Hence weight of chlorine present in a certain weight of silver

$$\text{chloride} = \text{Wt of AgCl} \times \frac{35{\cdot}5}{143{\cdot}5}$$

$$\text{Percentage of chlorine} = \text{Wt of AgCl} \times \frac{35{\cdot}5}{143{\cdot}5} \times \frac{100}{\text{Wt of sub}}$$

Similarly,

$$\text{Percentage of bromine} = \text{Wt of AgBr} \times \frac{80}{188} \times \frac{100}{\text{Wt of sub}}$$

$$\text{Percentage of iodine} = \text{Wt of AgI} \times \frac{127}{235} \times \frac{100}{\text{Wt of sub}}$$

Example 4. *0·1890 g of chlorine-substituted substance gave in a Carius determination 0·2870 g of silver chloride. What percentage of chlorine did the substance contain ?*

The whole of the chlorine present in the substance is converted into silver chloride. Also one molecule of silver chloride, AgCl (mol mass=108+35·5=143·5) contains one atom of chlorine (At mass=35·5), *i.e.*, 143·5 parts by weight of silver chloride contain 35·5 parts by weight of chlorine.

$$\text{or } 0{\cdot}2870 \text{ g of AgCl contains } 0{\cdot}2870 \times \frac{35{\cdot}5}{143{\cdot}5} \text{ g of chlorine}$$

$$\text{Wt of substance taken} = 0{\cdot}1890 \text{ g}$$

$$\therefore \text{Percentage of chlorine} = 0{\cdot}2870 \times \frac{35{\cdot}5}{143{\cdot}5} \times \frac{100}{0{\cdot}1890} = 37{\cdot}57.$$

8. Estimation of Sulphur.—The principle underlying Carius method for estimation of sulphur is essentially the same as in the estimation of halogens. It, however, differs from the one given above in fact that no silver nitrate crystals are taken in the bomb tube. Organic sulphur present is oxidised to sulphuric acid here. The contents of the tube are treated with barium chloride when a white precipitate of barium sulphate is obtained. This is washed, dried and weighed. One gram-molecular weight of barium sulphate, $BaSO_4$(137+32+64=233 g) contains 32 g of sulphur (At mass=32). From the weight of the barium sulphate precipitated, the percentage of sulphur in the organic compound is calculated as follows :

$$\text{Percentage of sulphur} = \text{Wt of } BaSO_4 \times \frac{32}{233} \times \frac{100}{\text{Wt of sub}}$$

Example 5. *0·2595 g of an organic substance in a quantitative analysis yielded 0·35 g of the barium sulphate. Calculate the percentage of sulphur in the substance.*

Weight of organic substance taken=0·2595 g

„ „ barium sulphate obtained=0·35 g

$$\text{Percentage of sulphur} = \text{Wt of } BaSO_4 \times \frac{32}{233} \times \frac{100}{\text{Wt of sub}}$$

$$= 0{\cdot}35 \times \frac{32}{233} \times \frac{100}{0{\cdot}2595} = 18{\cdot}52.$$

9. Estimation of Phosphorus.—The *Carius Method* for estimation of phosphorus is similar to that for sulphur. Here phosphorus present is oxidised to phosphoric acid which is precipitated from the contents with magnesia mixture. The precipitate of magnesium ammonium phosphate is ignited and magnesium pyrophosphate left as residue is accurately weighed.

$$\underset{\substack{\text{Magnesium}\\ \text{amm phosphate}}}{2MgNH_4PO_4} \longrightarrow \underset{\substack{\text{Magnesium}\\ \text{pyrophosphate}}}{Mg_2P_2O_7} + 2NH_3 + H_2O$$

One mole of magnesium pyrophosphate, $Mg_2P_2O_7$(48+62+112 =222g) contains 62 g of phosphorus.

$$\text{Hence percentage of phosphorus} = \text{Wt of } Mg_2P_2O_7 \times \frac{62}{222} \times \frac{100}{\text{Wt of sub}}$$

10. Micro-Analysis.—When only a few milligrams of an organic compound are available, micro-analysis has proved extremely helpful. It requires 3-5 mg of the substance for each estimation. Basic principles for various estimations are the same as discussed before. Weighings are done in a [illegible] microbalance sensitive up to 0·001 mg. In semi-micro method 20-25 [illegible] the substance is taken for each estimation.

QUESTIONS AND PROBLEMS

1. Describe, with the help of a diagram, the method of estimating carbon and hydrogen in an organic compound, indicating clearly the method of filling the combustion tube.

2. Describe Dumas method of estimating the percentage of nitrogen in organic compounds.

3. Describe in detail Kjeldahl's method for the estimation of percentage of nitrogen in an organic compound.

4. Describe Carius method for the estimation of (*i*) Phosphorus, (*ii*) Halogens and (*iii*) Sulphur.

Estimation of C, H and N (Dumas Method)

5. (*i*) 0·15 g of a base gave on ignition 0·3882 g CO_2 and 0·1160 g H_2O. (*ii*) Its 0·35 g gave 17·6 cm^3 of N_2 at NTP.

Calculate the percentage composition of the base.

6. An organic compound gave the following results on analysis :

(*a*) 0·73 g of the compound gave 1·32 g of carbon dioxide and 0·6 g of water.

(*b*) 0·365 g of the compound gave 56 cm^3 of nitrogen at NTP.

Calculate its percentage composition

Estimation of N (Kjeldahl's Method)

7. An organic compound gave the following results on analysis :

(*i*) 0·118 g of the compound gave on combustion 0·264 g of carbon dioxide and 0·162 g of water.

(*ii*) 0·354 g of the compound on treatment with Kjeldahl's method gave ammonia which was absorbed in 70 cm^3 of N/5-H_2SO_4. The excess of the acid required 40 cm^3 of N/5-NaOH for complete neutralization.

Calculate the percentage composition of the compound.

8. 0·2033 g of an organic compound gave on combustion 0·3780 g CO_2 and 0·1288 g H_2O.

0·257 g of this substance was digested with conc H_2SO_4, reaction mixture distilled with excess NaOH and the ammonia thus evolved was absorbed in 50 cm^3 of 0·1 N-HCl. The unreacted HCl then required 23·20 cm^3 of N/20-NaOH in volumetric estimation. Calculate the percentage composition.

Estimation of Halogens, S and P (Carius Method)

9. 0·301 g of an organic compound gave 0·282 g of silver bromide by halogen estimation method. Find the percentage of bromine in the compound.

10. 0·32 g of an organic compound containing sulphur was heated in a Carius tube and the sulphuric acid formed was precipitated as $BaSO_4$ with $BaCl_2$. The weight of dry $BaSO_4$ was 0·2334 g. Calculate the percentage of sulphur in the compound. [Ba=137·4]

11. 0·31 g of an organic substance was heated with fuming nitric acid in a Carius tube. The phosphoric acid formed was precipitated as $MgNH_4PO_4$ which on ignition left 0·148 g of $Mg_2P_2O_7$. Calculate the percentage of phosphorus in the organic substance.

ANSWERS

5. C=70·58% ; H= 8·59% ; N= 6·28% ; O=14·55%.
6. C=49·31% ; H= 9·59% ; N=19·18% ; O=21·92%.
7. C=61·01% ; H=15·25% ; N=23·73%.
8. C=50·71% ; H= 7·04% ; N=21% ; O=21·25%.
9. 39·867% 10. 10·00%. 12. 13·33%.

5

Determination of Molecular Weight

1. **Molecular Weight is a Number.**—*Molecular weight of a substance is the relative mass of the molecule as compared with the mass of an atom of carbon (^{12}C isotope) taken as 12 amu.* It is only a number. By saying that molecular weight of acetic acid ($C_2H_4O_2$) is 60, we mean that the molecule of acetic acid is 5 times as heavy as an atom of carbon.

Weight of a substance expressed in grams numerically equal to its molecular weight is termed its *gram-molecular weight* or *gram-molecule* or *mole*.

2. **Molecular Weights of Volatile Substances.**—Molecular weights of volatile liquids and solids can be easily determined by converting a known mass (say, w g) of the substance into vapour. The volume of the vapour obtained is measured under atmospheric conditions and then reduced to NTP (say, v cm^3). Therefrom the mass of 22,400 cm^3 of the vapour at NTP (gram molecular volume) is calculated. This gives the gram molecular weight.

Thus $$\text{Mol wt} = \frac{w \times 22{,}400}{v}.$$

3. **Victor Meyer's Method.**— In this method a known weight of the volatile substance is vaporized in a Victor Meyer's tube. The vapours obtained displace an equal volume of air into a graduated tube. The volume of air collected is measured and reduced to NTP.

4. **Molecular Weights of Non-volatile Substances.**—Every liquid freezes and boils at fixed temperatures and the effect of addition of a solute to it is such as to take the two fixed points farther from each other, *i.e.*, the melting point is lowered while the boiling point is raised. The depression of freezing point or elevation of boiling point is, however, found to be proportional to the amount of solute added to a known weight of the solvent. This is used in determination of molecular weights of non-volatile substances. The two methods employed are :

(*a*) **Depression of Freezing point or the Cryoscopic Method.** *Depression in freezing point of a solvent produced by dissolving 1 mole of any solute in 1000 g of the solvent is called its Molal Depression Constant* (K_f).

For example, molal depression constant of water = 1·86, *i.e.*, dissolution of 1 mole of any solute in 1000 g of water produces a depression of 1·86K in its freezing point.

The depression in freezing point ($=\triangle T$) noted experimentally by dissolving w g of the solute (mol wt$=m$) in W g of the solvent, is related to its molal depression constant, K_f as given below :

$$m=\frac{1000K_f\,w}{\triangle T\,W}$$

The molal depression constants for some common solvents are given below

Water $=1·86$
Acetic acid$=3·9$
Benzene$=5·12$
Phenol $=7·3$

Example 1. *1·5 g of a substance when dissolved in 60 g of water lowered the freezing point by 0·136 K. The molal depression constant for water is 1·86. Calculate the molecular weight of the substance.*

Putting down the data :

Weight of the substance (w)	$=1·5$ g.
,, ,, solvent (W)	$=60$ g.
Depression of freezing point ($\triangle T$)	$=0·136$ K
Molal depression constant (K_f)	$=1·86$
Molecular weight of the solute (m)	$=?$

Substituting these values in the relation :

$$m=\frac{1000K_f\,w}{\triangle T\,W}, \text{ we have}$$

$$m=\frac{1000\times1·86\times1·5}{0·136\times60}=341·9$$

$\therefore$ **Mol wt of the substance $=341·9$.**

(*b*) **Elevation of Boiling Point or Ebullioscopic Method.** *Elevation in boiling point of a solvent produced by dissolving 1 mole of any solute in 1000 g of the solvent is called its molal elevation constant* (K_b). For example, molal elevation constant of water is 0·52, *i.e.*, dissolution of 1 mole of any solute in 1,000 g of water produces an elevation of 0·52 K in its boiling point.

The elevation in boiling point ($\triangle T$) noted experimentally, by dissolving w g of the solute (mol wt.$=m$) in W g of the solvent, is related to its molal elevation constant, K_b as given below :

$$m=\frac{1000K_b\,w}{\triangle T\,W}$$

The molal elevation constants for some common solvents are given below :

Water $=0·52$
Benzene $=2·53$
Ether $=2·02$
Acetone $=1·71$
Chloroform $=3·63$
Ethyl alcohol $=1·22$
Acetic acid $=2·93$

Example 2. *The boiling point of pure acetone is 329·38 K at normal pressure. A solution of 0·707 g of a compound in 10 g of acetone boiled at 329·88 K. What is the molecular wight of the compound ?* (K_b *for acetone*$=1·67$)

7. Volumetric Method for Acids or Bases.—A known weight of the organic acid is dissolved in water or alcohol and titrated against a standard alkali. Knowing the volume of the alkali used, we calculate the weight of the acid (=y g., say) which requires 1,000 ml of a normal alkali solution for exact neutralization.

1,000 ml of the normal alkali contains one gram equivalent weight of the alkali and must, therefore, neutralize one gram equivalent weight of the acid (=y g here).

∴ Gram equivalent weight of the acid=y g

and Eq wt of the acid=y

Mol wt of the acid=Eq wt × basicity=$y \times n$.

In the case of organic bases, the known weight is titrated against a standard acid. Gram equivalent weight of the base is the weight of the base which needs 1,000 ml of the normal acid for exact neutralization.

Mol wt of the base=Eq wt × acidity.

Example 5. *0·0903 g of a tribasic acid dissolved in water neutralized 25·20 cm^3 of N/12 sodium hydroxide. Calculate the molecular weight of the acid.*

25·2 cm^3 of N/12-NaOH =0·0903 g of the acid

1000 cm^3 of N-NaOH $= \frac{0{\cdot}0903 \times 1000 \times 12}{25{\cdot}20}$

(Contains 1 gram eq wt of NaOH)

=43 g of the acid.

=1 gram equivalent weight of acid

Eq wt of the acid =43

Its molecular weight =Eq wt × basicity (=3 here)

=43 × 3=**129.**

Example 6. *0·183 g of a monoacid organic base requires 16 cm^3 of N/10-HCl for exact neutralizdtion. Calculate the molecular weight of the base.*

15 cm^3 of N/10-HCl=0·183 g of the base

1000 cm^3 of N-HCl= $\frac{0{\cdot}183 \times 1000 \times 1}{15}$

(Contains 1 gram eq wt of the acid)

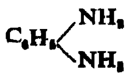
=122 g of the base

=1 gram eq wt of the base

∴ Eq wt of the base=122

Its molecular weight=Eq wt × acidity (=1 here)

=122 × 1=**122.**

To the Students. Common examples of a mono-acid base are $C_2H_5NH_2$, ethylamine and $C_6H_5NH_2$, aniline whereas  $C_6H_4(NH_2)_2$ phenylenediamine is a diacid base.

QUESTIONS AND PROBLEMS

1. How is the molecular weight of an organic substance determined ?

2. Describe a method for determination of molecular weight of (*i*) an organic base, and (*ii*) an organic acid.

Mol wt by VD Method

3. 0·067 g of a substance on vaporization displaced 25·4 cm^3 of air measured at NTP. Calculate the molecular weight of the substance.

Mol wt by Depression of FP Method

4. 13·6 g of a substance, when dissolved in 20 g of water, lowered its freezing point by 3·7 degrees. When one mole is dissolved in 100 g of water, the depression of freezing point is 18·5 degrees. Calculate the molecular weight of the substance.

5. 2·167 g of a substance dissolved in 100 g of benzene depressed the freezing point of benzene by 0·348K. What is the molecular weight of the substance ? Assume molal depression of freezing point of benzene to be 5 per 1,000 g of solvent.

Mol wt by Elevation of BP Method

6. 1·234 g of an organic compound when dissolved in 30·26 g of chloroform raised the boiling point by 1·210K. Calculate the molecular weight of the organic compound. Molecular elevation of boiling point for 100 g of chloroform is 37·86.

7. 0·3 g of camphor added to 25·2 g of chloroform raised the boiling point of the solvent by 0·229K. Calculate the molecular weight of camphor (K_b for 1,000 g of chloroform is 3·8).

Mol wt of Acids by Silver Salt Method

8 0·447 g of the silver salt of a dibasic acid gave 0·324 g of silver on ignition. Calculate the molecular weight of the acid.

9. The silver salt of a dibasic organic acid contains 71·05% of silver. Calculate the molecular weight of the acid.

Mol wt of Bases by Platinichloride Method

10. 0·300 g of the platinichloride of a mono-acid primary amine gave 0·09375 g of platinum on ignition. Calculate the molecular weight of the amine.

11. 0·596 g of platinichloride of a monoacid organic base left on ignition 0·195 g of platinum. Calculate the molecular weight of the base.

Mol wt by Volumetric Method

12. 0·177 g of a dibasic acid required 30 ml N/10-NaOH for neutralization. Calculate the molecular weight of the acid.

13. 0·2 g of a tribasic acid required for neutralization 27 ml of N/10-NaOH solution. Calculate the molecular weight of the acid.

14. 0·637 g of a tri-acid base required for exact neutralization 21·6 cm^3 of N/2-HCl. Calculate the mol weight of the base.

Miscellaneous

15. What is the minimum molecular weight that may be assigned to a compound which contains 38% sulphur ? (At wt of S=32).

ANSWERS

3. 59·09. **4.** 340. **5.** 311·3. **6.** 127·6.
7. 151·3. **8.** 104. **9.** 89·8. **10.** 107.
11. 93. **12.** 118. **13.** 222·2. **14.** 177·2.
15. 84·21.

6

Empirical and Molecular Formulae

1. **The Empirical Formula.**—Knowing the percentage composition and molecular weight of a substance, we proceed further to calculate its formula. The first step in this direction is the calculation of its simplest or empirical formula. *The simplest formula of a substance capable of expressing its percentage composition is called its* **Empirical or simplest formula**. It gives the *simple ratio existing* among the numbers of different kinds of atoms present in the molecule but does not indicate their *actual number*.

For example, CH_2O is the empirical formula of glucose and from it we can calculate its percentage composition. It gives us the simple ratio between atoms of the various elements present as C : H : O : : 1 : 2 : 1. Thus, as far as the present information goes, the glucose molecule may contain 1 atom of carbon, 2 of hydrogen and 1 of oxygen ; or 2 atoms of carbon, 4 of hydrogen and 2 of oxygen ; or any other multiple of the simple ratio expressed by the empirical formula.

2. **Calculation of Empirical Formula from Percentage Composition.**—We are given a box full of glass beads : 20% by weight being red each weighing 5 g, 30% by weight being yellow each weighing 10 g and the other 50% by weight being blue each weighing 25 g. *The relative number of red, yellow and blue beads can be easily found by dividing the percentage of each by its weight.*

Red$=20\div5=4$; Yellow$=30\div10=3$; Blue$=50\div25=2$.

Thus we see that for every 4 red beads, there are 3 yellow ones and 2 blue ones.

In a similar manner knowing the percentages of different elements in a molecule and their atomic weight, we can find the relative number of various atoms present therein. From these we can find the simplest whole number ratio between various atoms present and thus write the empirical formula of the compound.

Different steps involved in the calculation of the empirical formula of a chemical compound from its percentage composition are :

(*i*) Divide the percentage of each element by its atomic weight. This gives us *the relative numbers of atoms.*

(*ii*) Find the ratio of quotients by dividing each one by the smallest quotient. This is the *simplest ratio* existing among the various atoms present.

(*iii*) If the ratios are fractional, reduce them to the smallest possible whole numbers by multiplying throughout by a suitable integer. This gives the ***simplest whole number ratio.***

(*iv*) Write down the symbols of various elements present side by side with the above numbers as subscripts to the lower right corner of each. This gives the ***empirical or the simplest formula.***

3. **The Molecular Formula.**—*The formula which gives the actual number of atoms of various elements present in the molecule of the substance is termed its* **Molecular Formula.** It is either the same as the empirical formula of the substance or a simple multiple of it, *i.e.*,

$$\text{Molecular formula} = (\text{Empirical formula})_n,$$

where n is a whole number and is the ratio between the Molecular weight and the Empirical formula weight of the substance, *i.e.*,

$$n = \frac{\text{Molecular weight}}{\text{Empirical formula weight}}$$

For example, CH_2O is the Empirical formula for acetic acid, with Empirical formula weight = 30. Its molecular weight = 60

$$\therefore \qquad n = \frac{\text{Molecular weight}}{\text{Empirical formula weight}} = \frac{60}{30} = 2$$

and its *Molecular formula* is (Empirical formula)$_2$,

$$i.e., \ (CH_2O)_2 \quad \text{or} \quad C_2H_4O_2, \ (CH_3COOH)$$

Example 1. *An organic monobasic acid analysed as follows : (a) 0·1935 g gave 0·1320 g of CO_2 and 0·0270 g of H_2O ; (b) it contains 55·04% of chlorine ; (c) 0·2709 g of the acid dissolved in water neutralised 25·20 cm^3 of N/12 sodium hydroxide. Calculate the empirical and molecular formulae of the acid.*

(*i*) *Calculation of Percentage Composition* :

$$\text{Percentage of carbon} = \text{Wt of } CO_2 \times \frac{12}{44} \times \frac{100}{\text{Wt of substance}}$$

$$= 0{\cdot}1320 \times \frac{12}{44} \times \frac{100}{0{\cdot}1935} = 18{\cdot}6.$$

$$\text{Percentage of hydrogen} = \text{Wt of } H_2O \times \frac{2}{18} \times \frac{100}{\text{Wt of substance}}$$

$$= 0{\cdot}0270 \times \frac{2}{18} \times \frac{100}{0{\cdot}1935} = 1{\cdot}55$$

Percentage of chlorine = 55·04 (*given*)

Percentage of oxygen = (*by difference*)

$$= 100 - (18{\cdot}6 + 1{\cdot}55 + 55{\cdot}04) = 24{\cdot}81$$

(*ii*) ***Calculation of Empirical Formula*** :

Proceeding as usual and writing out various steps in a tabular form, we have :

Element	*Symbol*	*Percentage*	*At wt*	*Relative No. of atoms*	*Simple ratio*
Carbon	C	18·6	12	$\frac{18{\cdot}6}{12}=1{\cdot}55$	$\frac{1{\cdot}55}{1{\cdot}55}=1$
Hydrogen	H	1·55	1	$\frac{1{\cdot}55}{1}=1{\cdot}55$	$\frac{1{\cdot}55}{1{\cdot}55}=1$
Chlorine	Cl	55·04	35·5	$\frac{55{\cdot}04}{35{\cdot}5}=1{\cdot}55$	$\frac{1{\cdot}55}{1{\cdot}55}=1$
Oxygen	O	24·81	16	$\frac{24{\cdot}81}{16}=1{\cdot}55$	$\frac{1{\cdot}55}{1{\cdot}55}=1$

Hence the *Empirical formula* of the acid is **CHClO**.

(*iii*) *Calculation of Mol wt from the neutralization data* :

One gram eq wt of NaOH (present in 1000 cm³ of N-NaOH) must neutralize one gram eq wt of the acid.

25·20 cm³ N/12-NaOH $=0{\cdot}2709$ g of the acid.

1000 cm³ of N-NaOH $=\frac{0{\cdot}2709\times1000\times12}{25{\cdot}2}$

(*Containing 1 gram eq wt of NaOH*)

$=129$ g of the acid.

∴ Eq wt of the acid $=129$.

Its mol wt $=$ Eq wt $\times$ basicity $=129\times1=129$.

(*iv*) ***Calculation of Molecular Formula*** :

Empirical formula weight $=12+1+35{\cdot}5+16=64{\cdot}5$

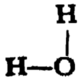
$$\frac{\text{Molecular weight}}{\text{Empirical formula weight}}=\frac{129}{64{\cdot}5}=2$$

Molecular formula is Empirical formula taken 2 times.

$=(CHClO)_2$ or $C_2H_2Cl_2O_2$

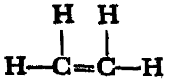
Being a monobasic acid, it must possess one —COOH group, *i.e.*, the molecular formula is **$CHCl_2COOH$** (*Dichloroacetic acid*).

4. **Structural Formula.**—Whereas the empirical formula of a compound gives the elements and the *relative number* of atoms in one molecule, the molecular formula gives the elements and the ***actual number*** of atoms. This, however, tells nothing about the internal arrangement of various atoms present. ***The formula showing how the various atoms are linked together is called the* Structural formula.** In a structural formula, the different valency bonds are represented by single or double lines as in the following examples :



$H{-}O{-}H$

Water



$H{-}CH{=}CH{-}H$

Ethylene

H—C≡C—H

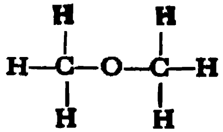
Acetylene

In the structural formula are summarised some very important properties of a chemical compound.

5. Rational Formula.—Writing down the structural formulae requires a lot of space and is very inconvenient in representing chemical reactions. *A shortened form of the structural formula is, therefore, used in practice and is called* **Rational formula.** Its superiority over the molecular formula lies in the fact that it gives an idea about the constitution of the compound. The linkages between carbon atoms are usually shown by dots. For example, dimethyl ether is represented as :

C_2H_6O ; Molecular formula

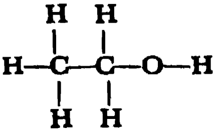
$(CH_3)_2O$ or $CH_3.O.CH_3$; Rational formula



$$\begin{array}{ccccccccc} & & H & & & & H & & \\ & & | & & & & | & & \\ H & - & C & - & O & - & C & - & H \\ & & | & & & & | & & \\ & & H & & & & H & & \end{array}$$

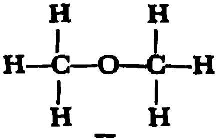
Structural formula

6. Determination of Structural Formula.—The molecular formula of a chemical compound is subjected to a systematic investigation of its chemical behaviour in order to assign a structural formula to it. The constituent atoms of the organic compounds are assigned their usual valencies and various possible structural formulae are constructed. In some cases only one structural formula is possible, for example, in the case of water, ethylene and acetylene as given above. If, however, in a certain case more than one formulae are possible, out of these the one which agrees with its chemical properties is selected as the correct one. For example, from the molecular formula C_2H_6O of ethyl alcohol, the two possible structural formulae are constructed as given below :



$$\begin{array}{ccccccccc} & & H & & H & & & & \\ & & | & & | & & & & \\ H & - & C & - & C & - & O & - & H \\ & & | & & | & & & & \\ & & H & & H & & & & \end{array}$$

I



$$\begin{array}{ccccccccc} & & H & & & & H & & \\ & & | & & & & | & & \\ H & - & C & - & O & - & C & - & H \\ & & | & & & & | & & \\ & & H & & & & H & & \end{array}$$

II

As ethyl alcohol gives the properties of hydroxyl group, structural formula I containing one —OH group is selected as the correct one.

This is the final stage of molecular diagnosis. Although it presents no particular difficulty in the case of simpler molecules, it is apt to involve a long and arduous investigation when complex substances are concerned. A fuller treatment of structural formula is given in a separate chapter towards the end.

Example 2. *Determine the molecular as well as the structural formulae of a compound from its following data :*

(*i*) *It contained* $C=16·27\%$, $H=0·68\%$ *and* $Cl=72·20\%$.

(*ii*) *0·2950 g of it displaced in a Victor Meyer's apparatus, 50·64 cm³ of moist air at 297K and 753·7 torr pressure.*

It forms addition products with sodium bisulphite, and yields chloroform when warmed with caustic soda solution (Vapour tension at 297K=22·2 torr) *(i) Calculation of the Empirical Formula from the percentage composition :* Proceeding as usual and writing out various steps in a tabular form, we have :

Element	Symbol	Percentage	At wt.	Relative No. of atoms	Simple ratio
Carbon	C	16·27	12	$\frac{16\cdot27}{12}=1\cdot36$	$\frac{1\cdot36}{0\cdot68}=2$
Hydrogen	H	0·68	1	$\frac{0\cdot68}{1}=0\cdot68$	$\frac{0\cdot68}{0\cdot68}=1$
Chlorine	Cl	72·20	35·5	$\frac{72\cdot20}{35\cdot5}=2\cdot03$	$\frac{2\cdot03}{0\cdot68}=3$
Oxygen (*by diff.*)	O	10·85	16	$\frac{10\cdot85}{16}=0\cdot68$	$\frac{0\cdot68}{0\cdot68}=1$

∴ ***Empirical formula*** of the compound is C_2HCl_3O.

Empirical formula weight$=24+1+106\cdot5+16=147\cdot5$.

(*ii*) ***Calculation of Molecular Weight*** :

$V_1=50\cdot64$ cm^3 $V_2=?$

$P_1=753\cdot7-22\cdot2=731\cdot5$ torr $P_2=760$ torr

$T_1=297$K $T_2=273$ K

Applying Gas Equation, volume of air displaced at NTP,

$$V_2=\frac{P_1V_1T_2}{T_1P_2}=\frac{731\cdot5\times50\cdot64\times273}{297\times760}=44\cdot80 \text{ cm}^3$$

Volume of vapour obtained = Volume of air displaced

= 44·80 cm^3 at NTP

Wt of 44·80 cm^3 of vapour at NTP = 0·2950 g (*Given*)

∴ Weight of 22·4 litres „ „ $=\frac{0\cdot2950\times22400}{44\cdot80}$

= 147·5 g

Hence, Mol wt of the compound = 147·5

(*iii*) ***Calculation of Molecular Formula*** :

As the molecular weight is the same as the Empirical formula weight of the compound, ***Molecular formula*** is identical with the Empirical formula, *i.e.*, it is C_2HCl_3O.

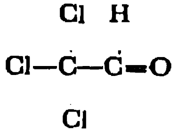
(*iv*) ***Determination of its Structural Formula*** :

As it forms an addition product with $NaHSO_3$, it contains an aldehyde (—CHO) group, *i.e.*, the formula is $CCl_3.CHO$—*chloral.*

When warmed with caustic soda solution, it gives chloroform according to the equation :

$$\underset{\text{Chloral}}{CCl_3\boxed{CHO\ +\ NaO}H} \rightarrow \underset{\text{Chloroform}}{CHCl_3} + \underset{\text{Sod. formate}}{HCOONa}$$

Hence *Structural formula* of the compound is



$$Cl-\underset{Cl}{\overset{Cl}{C}}-\overset{H}{C}=O$$

QUESTIONS AND PROBLEMS

Empirical Formula :

1. An organic compound, containing carbon, hydrogen, oxygen and nitrogen, on analysis gave the following values : Carbon=41·35%, Hydrogen=6·89% and Nitrogen=24·12%.

Find the simplest formula of the compound.

2. 0·45 g of an organic compound gave on combustion 0·792 g of CO_2 and 0·324 g of water. 0·24 g of the same substance was kjeldahlised and the ammonia formed was absorbed in 50 cm^3 of N/4-H_2SO_4. The excess acid required 77·0 cm^3 of N/10-NaOH for complete neutralization. Calculate the empirical formula of the compound.

Molecular formula from V.D. or Mol wt (given) :

3. 0·6 g of an organic substance containing only carbon, hydrogen and nitrogen gave on complete combustion 1·17 g carbon dioxide and 0·84 g water. With nitrous acid nitrogen was evolved. Identify the substance if its molecular weight is 45.

4. A compound on analysis gave the following percentage composition by weight : Hydrogen=9·09% ; Oxygen=36·26%, Carbon=54·55%.

Its vapour density is 44. Find the molecular formula of the compound.

Molecular Formula from Vapour Density Data :

5. The elementary analysis of an organic compound yielded the following results : C=39·98% ; H=6·72% and O=53·30%.

0·151 g of the compound on vaporisation displaced 33·8 cm^3 of air measured at 298K over water and at a barometric pressure of 745 torr. Determine its empirical and molecular formulae. (Vapour pressure of water at 298K=24 torr)

Molecular Formula of an Acid from Neutralization Data :

6. An organic monobasic acid gave the following results :

(*i*) 0·1 g gave 0·25245 g CO_2 and 0·0443 g H_2O on combustion.

(*ii*) 0·122 g of the acid required for neutralization 10 cm^3 of a N/10 alkali. Determine the molecular formula of the acid.

7. 0·2 gram of an organic monobasic acid gave on combustion 0·505 g of CO_2 and 0·692 g H_2O. 0·183 g of the acid required 15 cm^3 N/10 NaOH for neutralisation. Calculate the molecular weight and the molecular formula of the acid.

Molecular Formula from Silver Salt Data :

8. A dibasic organic acid containing 26·66% C and 2·22% H gave a silver salt containing 71·05% of silver. What is the formula of the acid ?

9. 0·236 gram of an organic dibasic acid gave on combustion 0·352 g of carbon dioxide and 0·108 g of water. 0·5 gram of its normal silver salt on being carefully ignited gave 0·32 gram of the pure silver. Assign a formula to the compound.

Molecular F of a Base from Platinichloride Data :

10. A monoacid organic base on analysis gave C=77·42%, H=7·53% and N=15·05%. 0·298 g of platinichloride left 0·0975 g of platinum. Calculate the molecular formula of the substance.

11. A monoacid base contains C=53·3%, H=15·5% and N=31·2%. 1·00 g of the chloroplatinate of the base gave 0·39 g of platinum on ignition. Calculate the molecular formula and also write down its structural formula.

Molecular Formula from Depression of FP Data :

12. The freezing point of the solution of 1·392 g of an organic acid C, assumed to be undissociated (in solution) in 20 g of water was found to be 271·89K (K_f for water=1·85). 0·177 g of the same acid neutralized exactly 12 cm^3 of a 0·2 N alkali. Calculate the basicity of the acid.

Molecular Formula from Elevation of BP Data :

13. 0·50 g of a non-volatile organic substance gave on combustion 0·88 g of carbon dioxide and 0·225 g of water vapour. 1·00 g of the substance when kjeldahlised produced 0·17 g of ammonia.

A solution of 1·25 g of the substance in 25 g of water boiled at 373·26K. Determine the formula of the compound. '*K*' the molecular elevation for 100 g of water being 5·2K.

Structural Formula :

Problems on Structural Formula can be attempted only after reading various organic compounds and their reactions. These have, therefore, been given in a separate chapter towards the end.

ANSWERS

1. C_2H_4NO. 2. $C_4H_5N_3O$. 3. $C_2H_5NH_2$ (*ethylamine*)
4. $C_4H_6O_2$ 5. CH_2O ; $C_4H_8O_4$. 6. $C_7H_6O_3$.
7. 122 ; $C_7H_6O_2$. 8. $(COOH)_2$. 9. $C_4H_6O_4$.
10. C_6H_7N. 11. C_2H_7N ; $C_2H_5NH_2$. 12. 2.
13. $C_4H_5NO_2$.

7

Structure of Organic Compounds

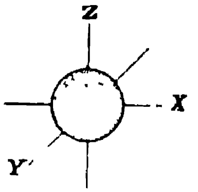
1. Atomic Orbitals.—The atom is made of certain fundamental particles called electrons, protons and neutrons and subatomic particles like positrons and mesons. It consists of a nucleus and one or more electrons grouped about it. According to the modern theory of atomic structure, hydrogen consists of a proton surrounded by an electron cloud in which there is the probability of finding the electron. The electron clouds are the modern substitutes for the orbits of the old Bohr-Sommerfeld model of the atom and are termed orbitals to show this relationship. *An orbital may be regarded as the region around the nucleus in which there is the probability of finding the moving electron.*

In quantum mechanics, an atomic orbital is defined as a one-electron wave function, ψ. For each point in space ψ^2 is proportional to the probability of finding an electron at that point. Such a *probability distribution* corresponds to the more useful concept of an *electron density distribution.* The mathematical function that describes this distribution has all the properties associated with waves. *It has a numerical magnitude* (its amplitude) *which may be positive or negative* (corresponding to a wave crest or a wave trough, respectively) *and nodes.* A node is a region where a crest and a trough meet. For the three-dimensional wave characteristic of electronic motion, the nodes are two-dimensional surfaces at which $\psi=0$.

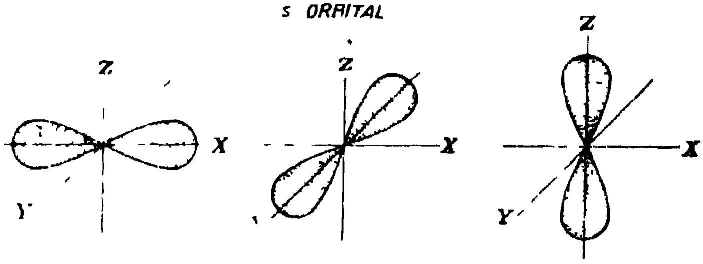
Atoms of heavier elements contain more than one electron which occupy definite orbitals. These orbitals are grouped about the nucleus in configuration roughly approximating to concentric shells. However, no two orbitals have both the same shape and size and the same location in space. Further, an orbital cannot be occupied by more than two electrons. The successive shells, starting nearest the nucleus, are numbered 1, 2, 3, 4, 5, 6, 7 (*Principal quantum numbers*) or designated as K, L, M, N, O, P and Q respectively. The electrons of a principal shell are most likely to be found in definite regions within each shell and these regions are termed **subshells**. These subshells are distinguished by their geometric shapes and the angular momentum which an electron will exhibit when present in these subshells.

The subshells are indicated by l, the *subsidiary quantum number* (also known as the *azimuthal quantum number*) which may have whole number values 0 to $n-1$. The subshells, having $l=0$, 1, 2 and 3 are also designated by letters *s*, *p*, *d* and *f* respectively. The number of subshells in a shell is equal to its principal quantum number. For example, 1 or K shell has only one subshell ($1s$), 2 or L shell has two subshells ($2s$ and $2p$) and 3 or M shell has three subshells ($3s$, $3p$ and $3d$). Similarly, four subshells in the 4 or N shell are the $4s$, $4p$, $4d$ and $4f$. The term $2p^4$ means that there are four electrons in the p subshell of the second or L shell. The maximum number of electrons which can be present in s, p, d and f subshells are 2, 6, 10 and 14 respectively.

Each subshell is made up of one or more orbitals. An orbital can have only two electrons, provided their spins are anti-parallel. Thus in the s-subshell having 2 electrons there is only one orbital and it is called s orbital. It must be borne in mind that an orbital is a particularly shaped space or volume within which electrons will be found. All s orbitals are spherical and are concentric about the nucleus (*see* Fig. 7·1).



s ORBITAL



p ORBITALS

Fig. 7·1—Geometrical representations of the *s* and *p* atomic orbitals.

The p-subshell with an electron population of six will have three orbitals which are designated as p orbitals. The three p orbitals are directed along the coordinate axes perpendicular to each other. Each orbital consists of two lobes lying along the axis, one on each side of the origin as represented in Fig. 7·1. The three p orbitals along the three axes are referred to by the notations p_x, p_y and p_z respectively. These have the same energy and are distinguished from each other only in direction. Similarly, there are five d orbitals and seven f orbitals. The arrangement of shells, subshells, and orbitals is illustrated schematically in Fig. 7·2.

In the geometrical representations of s and p orbitals in Fig. 7·1, the solid line represents the angular part of the wave function and defines a three-dimensional closed surface. As an approximation, we can regard the surface as a locus of points of constant value of

ψ such that certain proportion of electron density (fixed arbitrarily) is contained within the surface. For example, the value of ψ may be so selected that the resulting three-dimensional surface will enclose 80%, 90% or 95% (say) of the electron density.

Rules for distribution of electrons into various shells, subshells and orbitals. Based on the experimental data (mainly spectroscopic and magnetic) and theoretical considerations, various rules for distribution of electrons into various shells, subshells and orbitals are :

(1) The maximum number of electrons in any shell is $2n^2$ where n is the principal quantum number of the shell. Thus the maximum number of electrons in the first shell is 2 ; in the second 8 ; in the third 18 ; and in the fourth 32. Shells greater than the fourth never contain the maximum number of electrons, since there is not a sufficient number even in the heaviest atoms.

(2) The maximum number of electrons in a subshell is equal to $2(2l+1)$ where $l=0$ for *s*, 1 for *p*, 2 for *d* and 3 for *f*. Thus the maximum number of electrons which *s*, *p*, *d* and *f* subshells can have is 2, 6, 10 and 14 respectively.

(3) The electrons will always enter the available orbital of the lowest energy. As a working rule a new electron enters the orbital where $(n+l)$ is the minimum. When $(n+l)$ has the same value for two or more orbitals, the new electron enters the orbital where n is the minimum. This is known as **aufbau principle**. Thus a few orbitals arranged in the order of increasing energy are :

orbital :	1*s*,	2*s*,	2*p*,	3*s*,	3*p*,	4*s*,	3*d*,	4*p*,	5*s*
$(n+l)$ value :	1	2	3	3	4	4	5	5	5

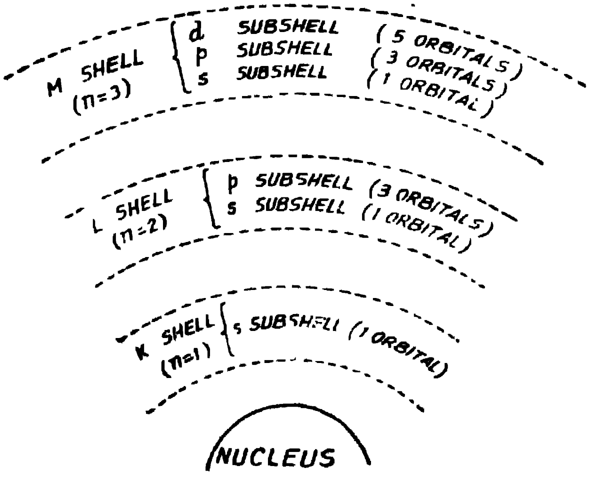


Fig. 7·2—Arrangement of shells and subshells in an atom.

(4) Only two electrons can be present in the same orbital, provided their spins are anti-parallel.

(5) Electrons never pair until no available empty orbitals are left to them (Hund's rule of maximum multiplicity). In other words, pairing begins only with the introduction of second electron in the *s*-orbital, the fourth electron in *p*-orbitals, the sixth electron in *d*-orbitals, and the eighth electron in *f*-orbitals. For example, two *p*-electrons in carbon are unpaired and three *p*-electrons in nitrogen are also unpaired. Pairing begins with the introduction of fourth electron in *p*-orbitals as in oxygen.

(6) Energy levels tend to become completely full, or exactly half full of electrons. Whenever energy levels are completely full and exactly half full, the element is more stable. For example, nitrogen with its *p*-orbitals half full is more stable than both of its neighbours, carbon and oxygen.

To illustrate the point further, filling of the three $2p$ orbitals in elements boron (at no=5) to neon (at no = 10) is given below :

Symbol	*At No*	*Electronic Configuration*	$1s$	$2s$	$2p_x$	$2p_y$	$2p_z$
Be	4	$1s^2\ 2s^2$	↑↓	↑↓			
B	5	$1s^2\ 2s^2\ 2p_x^1$	↑↓	↑↓	↑		
C	6	$1s^2\ 2s^2\ 2p_x^1\ 2p_y^1$	↑↓	↑↓	↑	↑	
N	7	$1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$	↑↓	↑↓	↑	↑	↑
O	8	$1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$	↑↓	↑↓	↑↓	↑	↑
F	9	$1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^1$	↑↓	↑↓	↑↓	↑↓	↑
Ne	10	$1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2$	↑↓	↑↓	↑↓	↑↓	↑↓

Electron distribution in elements beryllium to neon.

2. **The Nature of Bonds between Atoms.**—During a chemical change bonds between the atoms of reacting molecules are broken and new bonds between atoms are formed giving rise to molecules of products. It should, therefore, be worthwhile at this stage in our study of organic chemistry to examine the nature of different bonds formed between atoms.

The Lewis-Langmuir Concept of Stable Configuration. There are eight electrons in the outermost orbit of all noble gases except helium whose electrons (=2) are all in orbit 1. These enter into practically no reactions and form very few compounds. This condition of inactivity or maximum stability is evidently associated with their particular electronic arrangement. *The electronic arrangement in which eight electrons are present in the outermost orbit is called* **Stable configuration.** Of course, if the outermost orbit is the first one (as in helium), the number is *two*.

In the case of all other elements which show chemical activity, the outermost orbits are found to be incomplete. From this Lewis and Langmuir stated that in all cases *there is a general tendency for elements to enter into chemical reactions in such a way as to acquire stable configuration*. It would not be exaggeration to say that elements react with the main object to attain a stable configuration.

Electronic Theory of Valency. The electrons present in the outermost orbit of an atom determine the valency of that atom and are, therefore, called the **valency electrons**. If the valency electrons be removed, the remainder of the atom is called the **kernel** of the atom.

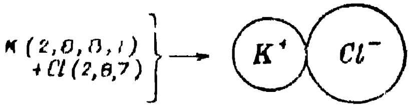
Formation of chemical compounds from elements involves either transference of valency electrons of one element to the outermost orbital of the other or sharing of the valency electrons of the two atoms. In either case a **chemical bond** is set up and as a result of it, both the atoms acquire a stable configuration.

Thus valency of an atom, according to the electronic theory of valency, is the number of electrons it can lend, borrow or share. A lending atom is called electro-positive, while a borrowing atom is called electro-negative.

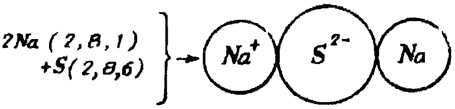
Three Types of Bonds. This tendency of the atom can be satisfied in three different ways and corresponding to these three ways there are three types of bonds :

(*i*) **Ionic Bond or Electrovalent Bond**. An ion is an atom or group of atoms which is charged due to the loss or gain of one or more electrons. When an atom gains an electron to form a negative ion (*anion*), it will increase in size. On the other hand, when an atom loses an electron to give positive ion (*cation*), it will contract. *The electron lost or gained is always from the outermost shell.*

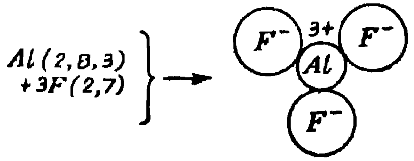
The ionic bond is formed due to the electrostatic attraction between stable ions formed by the complete transfer of electrons from one atom to another. The ions generally (though not always) have noble gas structure. These oppositely charged ions are held together by electrostatic attraction. For example, formation of KCl, Na_2S and AlF_3 can be explained as follows :



TH IONS ACHIEVE
ON STRUCTURE
(2,8,8)



Na^+ IONS ACHIEVE NEON STRUCTURE (2,8) AND S^{2-} ION ACHIEVES ARGON STRUCTURE (2,8,8)



BOTH Al^{3+} AND F^- IONS ACHIEVE NEON STRUCTURE (2,8)

The positive electrovalency is, therefore, numerically equal to the number of electrons an atom loses, and negative electrovalency is numerically equal to the number of electrons an atom gains, in order to acquire the stable electronic configuration of a noble gas with 8 electrons in the outermost orbit.

The formation of an ionic compound is obviously related to the ease of formation of the cations and anions from the neutral atom which depends on two major factors given below :

(*a*) *Ionization energy* (*I*). It is the minimum energy required to remove an electron from a gaseous atom in its ground state to form a gaseous ion.

$$M \rightarrow M^+ + e^- \;; \qquad \Delta H^\circ = I$$

Lower the value of ionization energy of an atom, greater will be the ease of formation of the cation from it.

(*b*) *Electron affinity* (*E*). It is the amount of energy released when an electron is added to a neutral atom, *i.e.*, energy of the reaction

$$X_{(g)} + e^- \rightarrow X^-_{(g)} \;; \qquad \Delta H^\circ = -E$$

Higher the electron affinity of an atom, greater the ease of formation of the anion from it.

Elements at the far left of the periodic table (*e.g.*, Li, Na, Mg) have relatively low ionization energy and are termed *electropositive*. Similarly, elements at the far right of the periodic table (*e.g.*, F, Cl, Br) have relatively high electron affinities and are termed *electronegative*.

Hence an ionic bond is formed between electropositive elements on far left and electronegative elements on far right of the periodic table.

Table 7·1—Abbreviated Periodic Table*

H							He
Li	Be	**B**	**C**	**N**	**O**	***F***	Ne
Na	**Mg**	Al	Si	*P*	**S**	**Cl**	**Ar**
						Br	
						I	

(*ii*) **The Covalent Bond.** For elements in the middle of the periodic table, too much energy is required to gain or lose sufficient electrons to form ions with complete octets. For example

$$\cdot\overset{\cdot}{\mathrm{B}}\cdot \rightarrow B^{3+} + 3e^- \;; \qquad I = 3641 \text{ kJ mol}^{-1}$$

$$\cdot\underset{\cdot}{\overset{\cdot\cdot}{\mathrm{C}}}\cdot \rightarrow C^{4+} + 4e^- \;; \qquad I = 6195 \text{ kJ mol}^{-1}$$

---

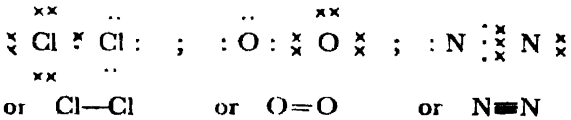
*More important elements are given in italics while the most important ones are given in bold type.

Consequently, such elements form molecules ***by sharing of one or more pairs of electrons in such a way that each atom acquires the configuration of the nearest noble gas and in general they tend to have paired electrons in all of their occupied orbitals.***

Similarly, linkage is set up between two electronegative atoms (*e.g.*, halogens) by sharing of electrons.

Structures of such compounds as water, methane, ethylene and acetylene can be explained in a similar manner by sharing of electrons. The idea of covalent bond was introduced by G.N. Lewis in 1916.

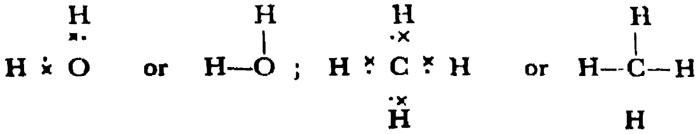
Single, double and triple covalent bonds. Covalent bonds may be formed by sharing one, two or three pairs of electrons and are termed single, double or triple covalent bonds respectively and are generally represented by single, double or triple lines. For example, molecules of chlorine, oxygen and nitrogen can be represented as follows :



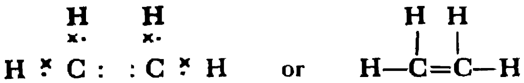
chlorine oxygen nitrogen

As a result of sharing, each of the atoms has completed its octet and assumed a noble gas configuration.

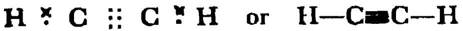
Similarly, electronic structures of water, methane, ethylene and acetylene (all covalent compounds) can be represented as follows :



Water Methane

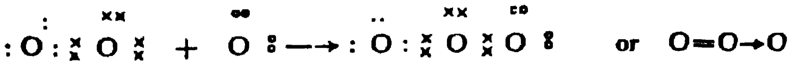


Ethylene (*with one double bond*)



Acetylene (*with one triple bond*)

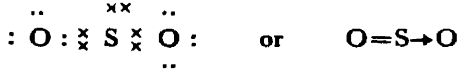
(*iii*) **Coordinate Valency** *by one-sided sharing of electrons.* In a molecule of oxygen octet of each oxygen is complete. If a new oxygen atom deficient by two electrons shares one electron pair belonging to one of the oxygen atoms of the molecule, it will have its octet completed. This is the formation of ozone molecule as shown below :



Oxygen molecule **Oxygen atom** **Ozone molecule**

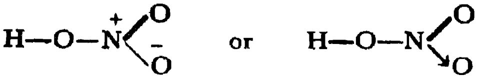
The electron pair shared is called lone pair, the oxygen atom of oxygen molecule is called the **donor**, while the new oxygen atom is the **acceptor**. The linkage set up is called a **coordinate linkage** or a **dative bond** represented by an arrow sign.

Sulphur dioxide is another example of compounds formed by coordinate linkage.



Sulphur dioxide molecule

A dative bond can be considered resulting from transfer of one electron from the donor to the acceptor. As a result of this transfer donor gets a unit positive charge and the acceptor a unit negative charge. Subsequently a covalent bond is set up due to sharing of one electron pair. Thus nitric acid can be represented in two ways :



Lewis Structures. The symbols used to discuss the systems given above are called *Lewis structures.* In addition to their being simple and convenient representations of ions and compounds, they help in accurate accounting for electrons. The following general rules should be borne in mind while writing Lewis structures :

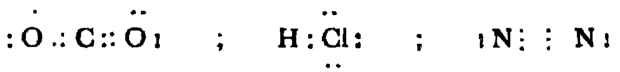
(1) *All valence electrons are shown.* Total number of such electrons is equal to the number contributed by each atom with an additional number added or subtracted to account for ionic charges, if any. For example, total number of electrons

for $CH_4 = 4(C) + 4 \times 1\ (H) = 8$

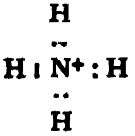
for $H_3O^+ = 3 \times 1\ (H) + 6\ (O) - 1$ (for $+1$ charge) $= 8$

for $NO_3^- = 5(N) + 2 \times 6\ (O) + 1$ (for -1 charge) $= 18$

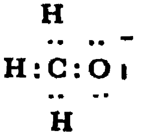
(2) *Each element should, to the maximum extent possible, have a complete octet. Hydrogen should have a complete duet.* For example, correct structures of CO_2, HCl and N_2 are :



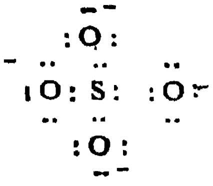
(3) **Formal charges** are assigned by dividing each bonding pair of electrons equally between the bonded atoms. The numbers of electrons belonging to each atom in this way is compared with the electrons originally belonging to the neutral atom and appropriate charges (+ or −) are assigned. Lone pairs belong to a single atom. For example,



ammonium ion



methoxide ion

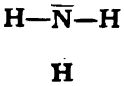


sulphate ion

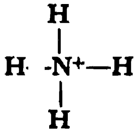
In NH_4^+ ion each electron pair around N atom is equally divided between N and H. This gives one electron for each H, the same as a hydrogen atom. N has a total of 4 electrons, *i.e.*, one less than the neutral nitrogen atom. Hence a formal charge of +1 is associated with N.

Similarly, formal charge on O in methoxide ion is −1. In SO_4^{2-} ion formal charge on S is +2 and on each O atom is −1.

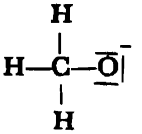
A further simplifying convention is to replace each shared pair of electron by a line and omit the lone pairs of electrons. For example,



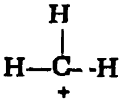
Ammonia



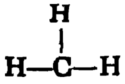
Ammonium ion



Methoxide ion



Methyl cation

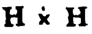


Methyl radical

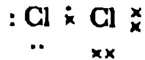
These simplified symbols are frequently called Kekule structures since these correspond to an earlier notational system proposed by Kekule.

Electrovalent compounds are generally non-volatile and insoluble in organic solvents. They are good electrical conductors in the fused state or in solution and have generally high melting points and high boiling points. Covalent compounds are generally volatile and usually soluble in organic solvents. They are non-electrical conductors and have generally low melting points and low boiling points. Coordinate compounds behave very much like covalent compounds but are usually less volatile.

3. **Polarity of Bonds.**—A covalent bond is set up by sharing of electrons between two atoms. It is further classified as *polar* or *non-polar* depending upon the fact whether the electron pair is shared unequally between the atoms or shared equally. For example, the covalent bonds in H_2 and Cl_2 are called non-polar as the electron pair is equally shared between the two atoms.



Hydrogen molecule



Chlorine molecule

(*Both formed by equal sharing of electrons between the atoms, i.e., by non-polar bonds.*)

In the case of hydrogen fluoride the bond is polar as the electron pair is unequally shared. Fluorine has a greater attraction for electrons (or *has higher electronegativity*) than does hydrogen and the shared pair of electrons is nearer the fluorine atom than hydrogen. The hydrogen end of the molecule, therefore, appears positive with respect to fluorine.

Arrangement of various atoms we are likely to encounter in organic chemistry in the decreasing order of electronegativity is :

$$F > O > Cl, N > Br > C, H$$

Bond polarities affect both physical and chemical properties of compounds containing polar bond. The polarity of a bond determines the kind of reaction that can take place at that bond and even affects the reactivity at nearby bonds. The polarity of bonds can lead to polarity of molecules and affect melting point, boiling point and solubility.

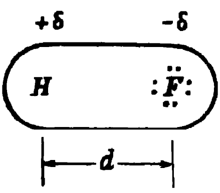


Fig. 7·4—A dipole.

A polar molecule like that of HF having two centres of charge is called a *dipole*. The degree of polarity in a polar compound is specified by its *dipole moment* (μ), which is equal to the *charge times the distance* between the positive and negative centres. Mathematically,

$$\underset{\text{in Debye units, D}}{\text{Dipole moment, }\mu} = \underset{\substack{\text{Electronic}\\ \text{charge in esu}}}{e} \times \underset{\substack{\text{Distance}\\ \text{in Angstroms}}}{d}$$

As e is of the order of 10^{-10} esu and d of the order of 10^{-8} cm μ is, therefore, of the order of 10^{-18} esu·cm and this unit is known as the Debye (D). Dipole moment is a vector quantity and is often indicated by an arrow parallel to the line joining the points of charge and pointing towards the negative end, *e.g.*, $\overset{+\!\!\longrightarrow}{\text{H—F}}$.

In general a polar bond is established between two atoms of different radii and different electronegativities when positive centres (nuclei) of different magnitudes combine to share an electron pair. Greater the value of the dipole moment, greater is the polarity of the bond.

The following points may be borne in mind in the study of organic chemistry :

(*i*) In the bond H—X, the hydrogen is the positive end of the dipole; *i.e.*, $\overset{+\!\!\longrightarrow}{\text{H—X}}$, wherein X is any atom other than H or C.

(*ii*) In the bond C—X, the carbon atom is the positive end of the dipole, *i.e.*, $\overset{+\!\!\longrightarrow}{\text{C—X}}$, wherein X is any atom other than carbon.

In the case of hydrocarbons both the direction and the value of the dipole are not constant and depend on the nature of hybridization. For example, in methane it is $\overset{+\!\!\longrightarrow}{\text{C—H}}$ and its value is 0·30 D while in ethylene it is $\overset{\longleftarrow\!\!+}{\text{C—H}}$ and its value is 0·40 D.

(*iii*) In case a molecule contains two or more polar bonds, its dipole moment is obtained by the vectorial addition of the dipole moment of the constituent bonds.

(*iv*) A symmetrical molecule is non-polar even though it contains polar bonds.

For example, carbon dioxide, methane and carbon tetrachloride, being symmetrical molecules, have zero dipole moments.

Dipole moment of methyl chloride is a vectorial addition of dipole moments of three C—H bonds and one C—Cl bond.

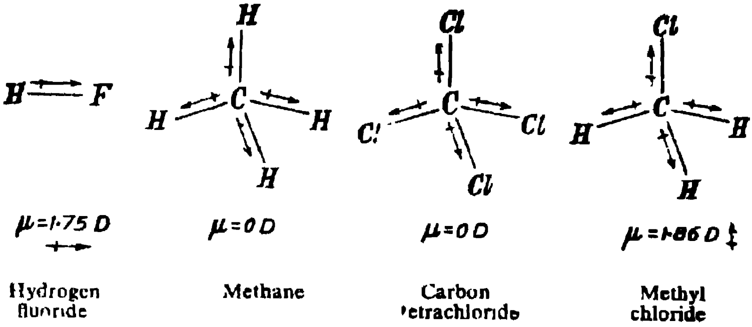


Fig. 7·5—Dipole moments of some molecules.

Not only do the polar bonds contribute to the dipole moment of a molecule, but also the lone pairs of electrons. For example, the dipole moment of nitrogen trifluoride ($\mu = 0{\cdot}21D$) is unexpectedly low. This is because magnetic moment due to unshared pair opposes vector sum of bond moments.

In ammonia the observed moment is probably due chiefly to the lone pair augmented by the sum of bond moments. Similarly two lone pairs of electrons contribute to the dipole moment of water, and indeed of any molecule in which they appear.

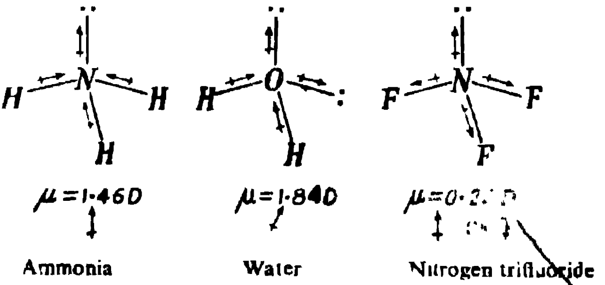


Fig 7·6—Contribution of lone pairs to dipole moments of some molecules

Dipole moments give a valuable information about the structure of molecules. For example, carbon dioxide is assigned a linear structure since its dipole moment is zero.

Problem. Which of the following compounds have a dipole moment? Comment giving diagrams and showing directions of various bond dipoles

Cl_2, HBr, CH_2Cl_2, $CHCl_3$, CH_3OH, $(CH_3)_2O$, $(CH_3)_2NH$, $BrCl$, BF_3, CO_2, CH_3COCH_3.

[**Hints**. (*i*) Cl_2, HBr, BrCl, CO_2 molecules are linear.

(*ii*) CH_2Cl_2, $CHCl_3$, CH_3OH, $(CH_3)_2O$, $(CH_3)_2NH$, molecules are tetrahedral with central atom in a state of sp^3 hybridisation.

(*iii*) BF_3 and $(CH_3)_2CO$ are planar with central atom in a state of sp^2 hybridisation

(*iv*) In $\overset{+\!\!\longrightarrow}{\text{Me—C}}$, $\overset{+\!\!\longrightarrow}{\text{Me—O}}$ and $\overset{+\!\!\longrightarrow}{\text{Me—N}}$ bonds Me is the positive end of the dipole.]

NATURE OF THE COVALENT BOND

4. **The Valence Bond Approach.**—To explain the nature of the covalent bond Heitler and London put forward the theory known as Valence Bond Approach in 1927. This was later on extended by Pauling and Slater in 1931. According to them :

(*i*) For a covalent bond to form, two atoms must be so located that an orbital of one *overlaps* an orbital of the other, each orbital containing a single electron.

(*ii*) When this happens, the two atomic orbitals merge to form a single *bond orbital* or a *localised molecular orbital* which is occupied by both electrons.

(*iii*) The two electrons that occupy a bond orbital must have opposite spins, *i.e.*, must be paired. Each electron has the entire bond orbital available to it and thus may be considered to belong to both the atomic nuclei.

(*iv*) As a result of overlapping there is maximum electron density somewhere between the two atoms. *A part of the binding force of covalent bond results from the electrostatic attraction between the nuclei and the accumulated electrons cloud between them.*

(*v*) Apart from this there is one other contributory factor in this force and that is *the neutralization of spin magnetic moments of the two electrons taking part in the bond formation.* This may be looked at as follows :

An electron is associated with the properties related to its spin. Direction of the spin is a determining factor in bond formation. Although the statement is often made that an electron has a spin, what it really means is that an electron has a magnetic moment. When two electrons are paired, these are so oriented that their magnetic fields cancel one another and develop attraction forces. Conversely, two electrons with parallel spins would repel each other. *Thus for a stable bond formation, the condition is that the electrons should have opposite spins.*

What gives the covalent bond its strength ? *The arrangement of electrons and nuclei in a molecule contains less energy and is, therefore, more stable than the arrangement in the isolated atoms.* Formation of a bond is, therefore, always accompanied by evolution of energy. Amount of energy (per mole) that is given off when a bond is formed (or energy required to break the [illegible]ed *bond dissociation energy.*

Pauling and Slater extended the above theory to account for the direction of the covalent bond which arises due to the vectorial nature of charge intensities considered responsible for such bonding. According to them :

(*i*) *The strength of chemical bond is proportional to the extent of overlapping of the electron orbitals.*

(*ii*) *The overlapping of the orbitals] of only those electrons which take part in the bond formation, would occur.*

(*iii*) *Between two orbitals of the same stability* (*i.e.*, *having same energy*), *one more directionally concentrated would form a stronger bond.*

(*iv*) A spherically symmetrical orbital, *e.g.*, *s* orbital, will not show any preference in direction whereas non-spherical orbitals, *e.g.*, *p* or *d* orbitals, will tend to form a bond in the direction of maximum electron density within the orbital.

Types of Overlapping and Orbital Diagrams. Different types of overlapping which we come across are :

(1) *s-s Overlapping.* Hydrogen atom has only one electron ($1s^1$) and is therefore, available for bonding. In the formation of a molecule of hydrogen spherical $1s$ orbital of one overlaps with that of the other (Fig. 7·7) forming a single covalent bond.

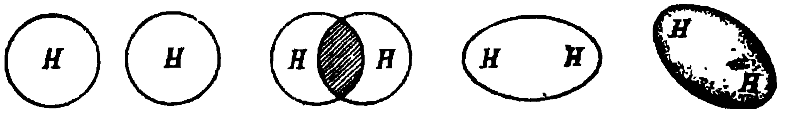


Fig. 7·7—Overlap of *s-s* orbitals.

For hydrogen the system is most stable when the distance between the nuclei is 0·74 Å (1 angstrom$=10^{-8}$ cm). At this distance the stabilizing effect of overlapping is exactly balanced by repulsion between similarly charged nuclei. This distance is termed *bond length.* The resulting hydrogen molecule contains 453·1 kJ mol^{-1} less energy than the hydrogen atoms from which it is made. We can say that H—H bond has a length$=$0·74Å and strength$=$453·1 kJ.

The bond orbital is sausage-shaped with its long axis lying along the line joining the nuclei. It is symmetrical about the long axis.

Electronic configuration of lithium is $1s^2$, $2s^1$. In the formation of Li_2 molecule Li—Li bond is set up due to the overlapping of their $2s$ orbitals. Similarly, in the LiH molecule Li—H bond is due to overlapping of the $2s$ orbital of lithium and $1s$ orbital of hydrogen.

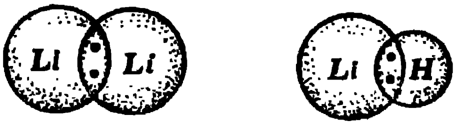


Fig. 7·8—Orbital diagrams for Li_2 and LiH molecules produced as a result of *s-s* overlapping.

(2) *s-p Overlapping.* Electronic configuration of fluorine atom is $1s^2$, $2s^2$, $2p_x^2$, $2p_y^2$, $2p_z^1$ having one

of the electrons ($2p_z$) unpaired. The molecule of hydrogen fluoride (H—F) is produced by the overlapping of 1s orbital of hydrogen with $2p_z$ orbital of fluorine (s-p overlapping).

Similarly, the molecule of lithium fluoride (Li—F) is produced by the overlapping of 2s orbital of lithium with the $2p_z$ orbital of fluorine.

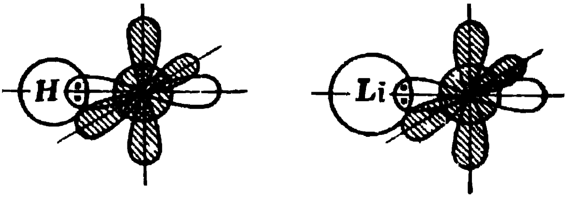


Fig. 7·9—Molecules of HF and LiF produced as a result of *s-p* overlapping

(3) *p-p Overlapping.* The electronic configuration of chlorine is $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p_x^2$, $3p_y^2$, $3p_z^1$ with one electron ($3p_z$) being unpaired. The molecule of chlorine is produced by the overlapping of the $3p_z$ orbitals of two atoms.

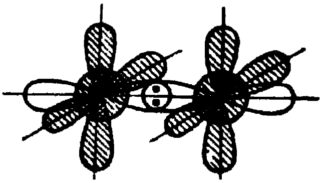


Fig. 7·10—Formation of Cl—Cl molecule by the overlapping of their $3p_z$ orbitals

Formation of F—F and Br—Br molecules can be explained in a similar manner.

Following this concept of overlapping of orbitals, the structure of water (H_2O) and ammonia (NH_3) molecules can be discussed. The arrangement of electrons in nitrogen and oxygen atoms is :

Nitrogen	$1s^2$, $2s^2$, $2p^3$
Oxygen	$1s^2$, $2s^2$, $2p^4$

Following Hund's rule (page 1·58), the above electronic arrangement can be represented as :

Nitrogen	$1s^2$, $2s^2$, $2p_x^1$, $2p_y^1$, $2p_z^1$
Oxygen	$1s^2$, $2s^2$, $2p_x^2$, $2p_y^1$, $2p_z^1$

Nitrogen thus has three unpaired electrons while oxygen has two. It is for this reason that the former exhibits a valency of three and oxygen has a valency of two.

When the nitrogen atom combines with three hydrogen atoms to form a molecule of NH_3, the three N—H bonds should be at right angles to one another. In the same way the two O—H bonds in the formation of water should be at right angles to each other. The two structures are shown diagrammatically in Figs. 7·11 and 7·12. The NH_3 molecule shows a pyramidal structure.

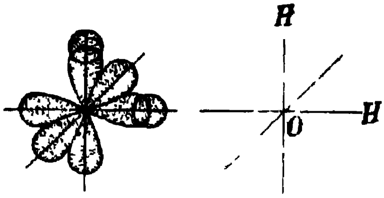


Fig. 7·11—Diagrammatic representation of the directed bonds in the water molecule

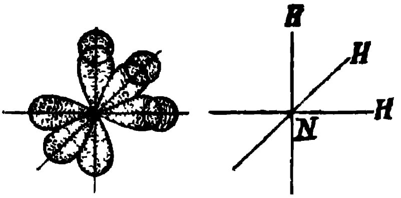


Fig 7·12—Diagrammatic representation of the directed bonds in the ammonia molecule.

Actually the angle between O—H bonds in H_2O is 105° instead of 90° and between N—H bonds in NH_3 108° instead of 90°. The same can be explained on the concept of hybridization discussed later.

Sigma and Pi Bonds. According to the valence bond approach, a bond is set up due to overlap of atomic orbitals of the two combining atoms. A strong or weak bond is obtained depending upon the extent of overlapping. When an overlapping of *s-s*, *s-p* and *p-p* atomic orbital occurs, a new ***bond orbital*** or ***localised molecular orbital*** having a pair of electrons with opposite spins is formed.

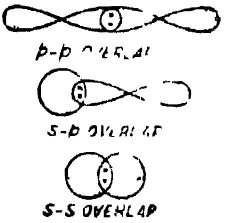


Fig. 7·13—Overlapping of *s-s*, *s-p* and *p-p* orbitals forming sigma bonds.

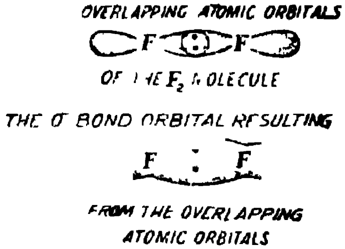


Fig. 7·14—Shape of the molecular orbital produced by *p-p* overlapping of atomic orbitals of fluorine forming sigma bond.

Since the two electron clouds overlap along their axes, maximum overlap is possible. Hence the bond formed is a strong bond. The bond orbital is symmetrical about the line joining the two nuclei.

Bond orbitals which are symmetrical about the line joining the two nuclei are termed σ-bonds (sigma bonds). These are strong bonds formed as a result of maximum overlapping of s-s, s-p or p-p orbitals along their axes.

Electronic configuration of nitrogen being $1s^2$, $2s^2$, $2p_x^1$, $2p_y^1$, $2p_z^1$, there are three unpaired electrons in each nitrogen atom. When two atoms of nitrogen combine to form a nitrogen molecule (N_2), one of the unpaired electrons of each nitrogen atom is shared. There is an overlapping of p_x orbitals of the two atoms along the axes forming a sigma bond as shown in Fig. 7·15. The other two p-orbitals, each containing one electron, are at right angles to each other and also to the plane of the sigma bond and overlap as shown in Fig. 7·16.

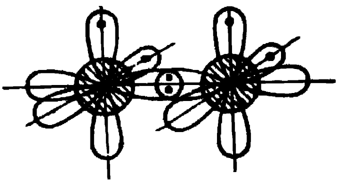


Fig. 7·15—Two atoms of nitrogen joined by a sigma bond due to p-p overlapping.

Since these p-orbitals can overlap only sideways (lateral overlapping), the overlapping is only partial and the bond produced is a weak bond (*cf.* sigma bond which is produced by maximum overlap along the axes and is a strong bond). *The bond formed by the sideways overlap of p-orbitals is called a* **Pi** (π) *bond.* Electron cloud of a *pi* bond is unsymmetrical and is concentrated above and below the plane of the sigma bond. In the molecule of nitrogen the triple bond linking the two nitrogen atoms is a combination of one sigma bond and two *pi*-bonds. The orbital diagram of nitrogen molecule is shown in Fig. 7·17.

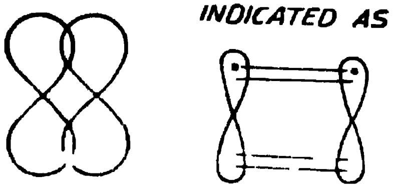


Fig. 7·16—A *pi* bond formed by the sideway overlap of p-orbitals.

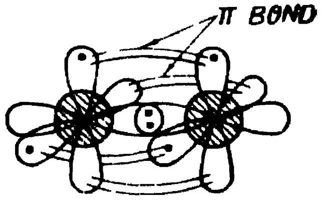


Fig. 7·17 – Orbital diagram of nitrogen molecule (N≡N) in which there are one sigma and two *pi* bonds linking the nitrogen atoms.

5. **Geometry of Molecules and Hybridisation.**—Consider the formation of methane (CH_4). Carbon has the configuration

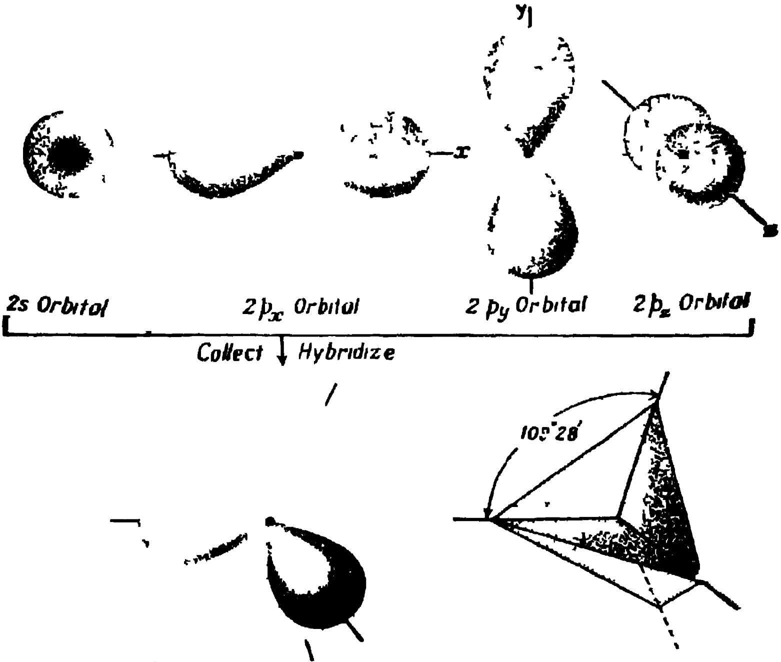
$$1s^2, 2s^2, 2p_x^1, 2p_y^1.$$

There being only two unpaired electrons, carbon should have a valency of 2. But in very few compounds of carbon, its bivalency is exhibited. To explain the tetravalency of carbon which is most common in its large number of compounds, one must think that two $2s$ electrons are unpaired and one of these is excited to $2p_z$ state. The configuration that would result now would be

$$1s^2, 2s^1, 2p_x^1, 2p_y^1, 2p_z^1$$

There being four unpaired electrons, this configuration would give rise to four bonds, three ($2p$ orbitals) of which would be at right angles to one another and the fourth ($2s$ orbital) will not have any preferential direction. Again three dumb-bell shaped p electron clouds would form stronger bonds than the one spherically symmetrical s-electron because dumb-bell shaped orbitals can overlap more than the spherical orbitals. The reality is, however, different. The four C—H bonds in methane are equivalent, that inclined at at an angle of 109° 28′.

To explain this it is assumed that the four orbitals 2s, $2p_x$, $2p_y$ and $2p_z$ can be mixed or hybridised to produce four new orbitals equivalent to each other in all respects This process is called **Hybridisation** and the four new orbitals produced as a result of hybridisation are termed *hybridised orbitals* These subtend an angle of 109° 28′ with each other and are directed towards the corners of a regular tetrahedron as shown in Fig 7 18 The equivalence of the four valencies of carbon is thus accounted for Since the hybridisation has taken place by combining one *s* and three *p* wave functions in the above case, it is called sp^3 (read *sp* three) *hybridisation* Since the four equivalent orbitals are arranged tetrahedrally, it is also termed as *tetrahedral hybridisation*. The hybridised bonds are stronger than the original *s* or *p* electron bonds.



Four sp^3 hybrid atomic orbitals with common origin

Tetrahedral hybridisation axes of sp^3 hybrid orbitals

Fig 7 18—Hybridisation of atomic orbitals in carbon atoms (sp^3 *hybridisation or Tetrahedral hybridisation*).

In methane each of the four C—H bonds is formed by the overlap of carbon sp^3 hybrid orbital with 1*s* orbital of each hydrogen atom

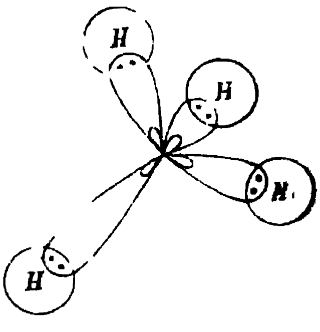


Fig 7·19 —Orbital diagram of methane molecule

Promotion of the electron from the $2s$ to the $2p$ level requires energy, but the liberation of energy and consequent increase in stability gained by the formation of four covalent bonds, supplies even more energy than is required for promotion of the electron. The process is schematically illustrated in Fig. 7·20.

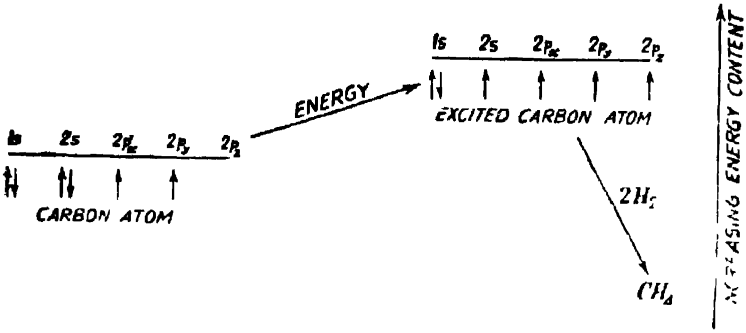


Fig. 7·20—In stable molecules carbon always forms four bonds.

Now let us consider the formation of boron trichloride (BCl_3) Electronic configuration of boron (At. No.=5) is

$$1s^2, 2s^2, 2p_x^1.$$

There being only one unpaired electron boron should be monovalent. But actually boron is trivalent as in BCl_3. The formation of three covalent bonds is explained by thinking that the two $2s$ electrons are unpaired and one of these is excited to $2p$ state which results in the configuration

$$1s^2, 2s^1, 2p_x^1, 2p_y^1.$$

The three half-filled orbitals hybridise to give three hybridised sp^2 read sp two orbitals mutually inclined at an angle of 120°.

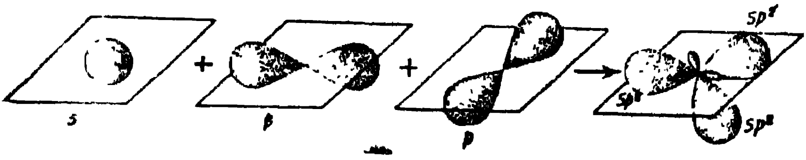


Fig. 7·21—Hybridisation of boron orbitals.
(sp^2 hybridisation or Trigonal hybridisation)

Fig. 7·21 gives a pictorial illustration of the sp^2 hybridisation. Simple p orbitals have two regions in space in opposite direction of the nucleus. In sp^2 orbitals one of these regions has shrunk while the other has expanded showing that now the electron density is primarily in this latter region.

The hybrid orbitals are inclined at an angle of 120° to one another. In boron trichloride each of the three B—Cl bonds is formed by the overlap of a boron sp^2 orbital with a chlorine orbital giving finally a planar molecule with 120° bond angles.

An extremely important concept of **bond angle emerges here.** Four sp^3 hybrid orbitals are tetrahedrally inclined at an angle of 109·5° whereas sp^2 hybrid orbitals are planar and inclined at 120°. **Bond angle** is governed by Pauli's exclusion principle and ***is due to the tendency of the unpaired electrons to get as far from each other as possible.*** Knowing this we can predict that angle between two *sp* hybrid orbitals must be 180° as discussed in case of acetylene on page 1·74.

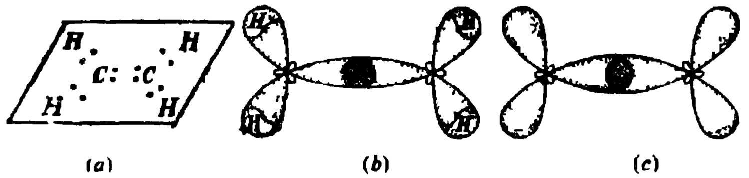
In the light of hybridisation, we can satisfactorily explain the structure of ethylene and acetylene

To form the bonds required in ethylene, three orbitals (one *s* orbital and two *p* orbitals) of each carbon atom coalesce (hybridise), *i.e.*, combine to form identical orbitals, each called an sp^2 orbital Fig. 7 21)

The three sp^2 orbitals differ only in direction. They lie in the same plane and are mutually inclined at 120° The carbon atom becomes

$$C(sp^2)^1, (sp^2)^1, (sp^2)^1, p^1$$

i.e., its four valence electrons are placed one in each orbital of the new hybridised atom In the molecule of ethylene (C_2H_4) two carbon atoms are joined to each other by a sigma bond formed by overlap of sp^2 with sp^2 orbital The four C—H bonds are sigma bonds each resulting from the overlap of sp^2 orbital of carbon with *s* orbital of hydrogen, as shown in Fig 7 22 Each one of these five bonds has a symmetrical distribution of the electron cloud linked with it and is termed a *sigma* (σ) *bond* A σ bond is formed by the overlap of an *s*-orbital in any direction or the overlap of *p*- or hybrid orbitals in the direction of inter nuclear axis



(*a*) (*b*) (*c*)

Fig 7 22 -The sigma bond skeleton in ethylene (*a*) Electronic formula, (*b*) Formation of five sigma bonds by s-sp^2 overlap (in the case of four C—H bond) and sp^2—sp^2 overlap (in case of C—C bond), (*c*) Resultant molecular orbitals

After formation of sigma bonds there remains on each carbon atom one unhybridised *p*-orbital perpendicular to the plane of the C—H and C—C bonds The second bond between the carbon atoms can be formed by the ***sideways overlap*** of these *p*-orbitals as shown in Fig. 7·23 wherein sigma bonds have been represented by straight lines

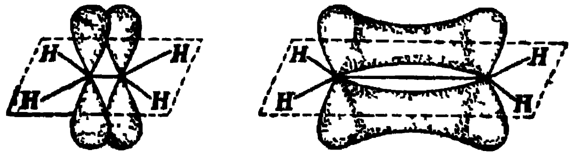


Fig 7·23—The *pi* bond in ethylene

Electron cloud of the bond is unsymmetrical and concentrated above and below the plane of carbon and hydrogen atoms. This bond is termed as a *pi* (π) *bond*. The orbital arrangement is like a "hot dog".

The so-called double bond between two carbon atoms is thus a combination of one *sigma* and one *pi* bond.

Similarly, to form the bond required in acetylene two orbitals (one *s* orbital and one *p* orbital) of each carbon atom hybridise to form two identical orbitals each called an *sp* orbitals (Fig. 7·24).

2s

2p ORBITAL

TWO Sp-HYBRID ATOMIC ORBITALS WITH COMMON ORIGIN

Fig. 7·24—*sp* hybridisation or Digonal hybridisation.

The two *sp* orbitals are linear and the carbon atom becomes

$$C(sp)^1, (sp)^1, p_y^1, p_z^1.$$

One *sp* orbital forms a sigma bond with a hydrogen atom and the other with the neighbouring carbon atom (Fig. 7·25).

(*a*) (*b*)

Fig. 7·25—The sigma bond skeleton in acetylene: (*a*) Formation of three sigma bonds by *s*-*sp* overlap (in the case of 2 C—H bonds and *sp*-*sp* overlap (in the case of C—C bond); (*b*) Resultant molecular orbitals.

After formation of the sigma bonds there remain with each of the two carbon atoms two electrons, one in each of two unhybridised *p* orbitals. These two *p* orbitals are perpendicular to one another and perpendicular to the sigma bond between them. Each pair of these *p* orbitals forms a *pi* bond by sideways overlap as shown in Fig. 7·26 wherein the sigma bonds are represented by straight lines.

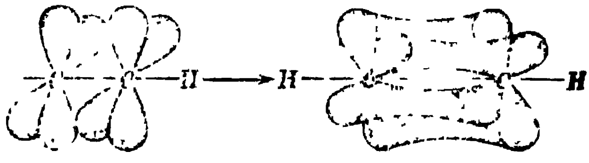


Fig. 7·26—Two *pi* bonds in acetylene.

The configuration corresponds to a hypothetical hot dog with two buns.

When electrons of any atom have been placed in hybridised orbitals, the atom is said to be in a *valence state*. The atom on its own cannot exist in a valence state and energy is required to promote the atom to this condition. This energy is obtained through the formation of bonds which are stronger with the hybridised orbitals than with 'pure' orbitals, *i.e.*, more energy is released with the former than with the latter.

6. Effectiveness of Overlap.—The strength of a covalent bond is determined by the degree of overlap of the two orbitals forming a bonding or localised molecular orbital. The following points will be helpful in predicting the strength of a covalent bond :

(*i*) Bonding between two *s* orbitals is weak particularly when two orbitals are at different energy levels (*e.g.*, Li and K). Strongest bond between *s* orbitals is between two 1*s* orbitals as in hydrogen.

(*ii*) The more *s* character a hybrid orbital has, the weaker is its bonding strength.

(*iii*) A strong sigma bond is formed by the end-on overlap of two *p* orbitals at the same energy level. The bond is much weaker if the orbitals have different principal quantum numbers and the bond energy approaches zero as the distance between the two levels increases. For example, C—Br bond in bromobenzene is much weaker than C—F bond in fluorobenzene.

(*iv*) The sideways overlapping of two *p* orbitals is much less effective and results in weak bonding.

7. Molecular Orbital Theory.—In the *valence bond approach* a bond is formed between two atoms when they are brought together close enough to ensure maximum overlap of the atomic orbitals. When the bond is formed only one electron from each bonded atom loses its identity and moves in the outer atomic orbitals of both bonded atoms. The inner atomic orbitals from each atom forming the bond are, however, undisturbed, *i.e.*, each atom retains its own identity.

According to the *molecular orbital theory*, the orbitals are associated with the molecule as a whole. The quantized molecular orbitals of varying energy levels surround both the nuclei of the bonded atoms. These molecular orbitals are formed by the coalescence of the individual atomic orbitals when the atoms to be bonded come together. The orbitals of the bonded atoms lose their individual identity. The configuration of the molecule is obtained by entering electrons into these quantized molecular orbitals in an *aufbau* order analogous to that employed in the filling of atomic orbitals. Corresponding to the practice of indicating atomic orbitals by the letters, *s*, *p* and *d*, molecular orbitals are assigned similar Greek letter designations σ (sigma), π (pi), δ (delta).

Two atomic orbitals, one from each bonded atom, whose energies are comparable in value and which possess a large amount of overlap, coalesce to form two molecular orbitals. One of these molecular orbitals is lower in energy than either of the atomic orbitals from

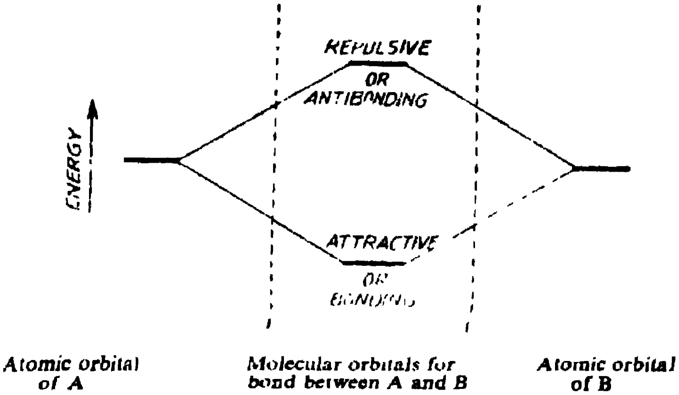


Fig. 7·27—The formation of two molecular orbitals from the coalescence of two atomic orbitals in atoms A and B.

which it was formed and hence gives rise to an attractive state as depicted in Fig. 7·27. The other molecular orbital is higher in energy and, therefore, gives rise to a repulsive state. This high energy molecular orbital is termed the *anti-bonding orbital* since electrons placed

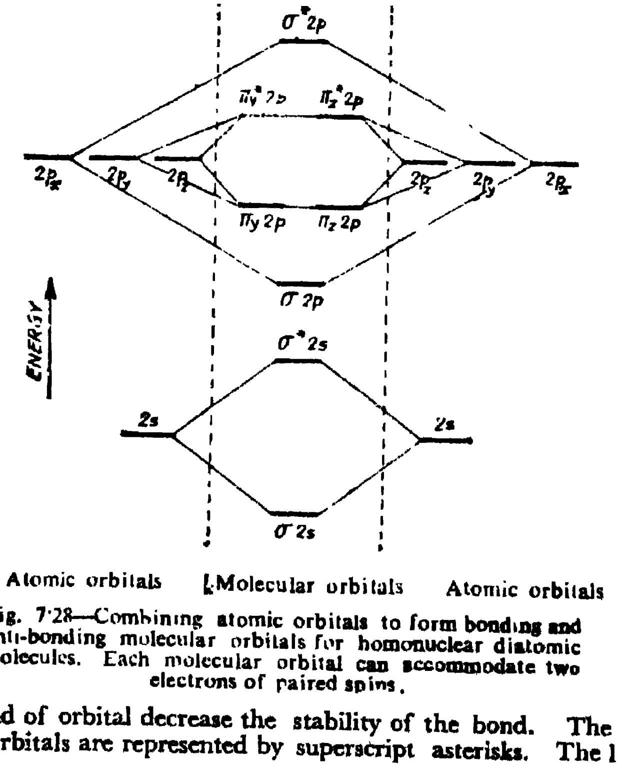


Fig. 7·28—Combining atomic orbitals to form bonding and anti-bonding molecular orbitals for homonuclear diatomic molecules. Each molecular orbital can accommodate two electrons of paired spins.

n this kind of orbital decrease the stability of the bond. The anti-onding orbitals are represented by superscript asterisks. The lower energy molecular orbital is called ***bonding orbital***, since electrons placed in such an orbital increase the stability of bond.

The molecular orbitals for homonuclear diatomic molecules formed from given atomic orbitals are designated as follows* :

$\sigma 1s$,	$\sigma^* 1s$	formed	from	$1s$	atomic	orbitals
$\sigma 2s$,	$\sigma^* 2s$	,,	,,	$2s$	,,	,,
$\sigma 2p$,	$\sigma^* 2p$	,,	,,	$2p_x$	,,	,,
$\pi_y 2p$,	$\pi_y{}^* 2p$	,,	,,	$2p_y$	,,	,,
$\pi_z 2p$,	$\pi_z{}^* 2p$	,,	,,	$2p_z$	,,	,,

These molecular orbitals are shown schematically in an energy level diagram in Fig. 7·28.

Significance of Bonding and Antibonding Molecular Orbitals To understand the significance of bonding and antibonding molecular orbitals in terms of wave functions it is necessary to know the electronic charge distribution of these orbitals. A simple method for this consists in the derivation of molecular orbitals by the *linear combination of atomic orbitals* (LCAO method).

Each atomic orbital is described by a wave function ψ. According to LCAO method, the molecular orbital wave function ψ_{MO} is a linear combination (addition or subtraction) of the wave functions of the individuals (ψ_A and ψ_B), *i.e.*,

$$\psi_b = \psi A + \psi B \qquad \text{.. (1)**}$$

$$\psi_a = \psi A - \psi B \qquad \text{.. (2)}$$

Squaring Eqn. (1), we get

$$\psi^2{}_b = \psi^2 A + 2\psi A\ \psi B + \psi^2 B \qquad \text{.. (3)}$$

It may be recalled that the term ψ^2 represents charge density. Therefore, ψ^2 A and ψ^2B represent charge densities of the isolated atoms while $\psi^2{}_b$ stands for the charge density between the two atoms bonded in the molecule.

Obviously greater the value of $\psi^2{}_b$, greater is the charge density between the two atomic nuclei and stronger the bond between them. It is seen from equation (3), that charge density of the molecular orbital ($\psi^2{}_b$) is greater than the sum of charge densities of the two isolated atoms ($\psi^2 + \psi^2$B) by a term 2ψAψB.

This term exists as a result of the *interaction* or *overlap* of atomic orbitals. Larger the overlap, greater the charge density between the nuclei and more stable

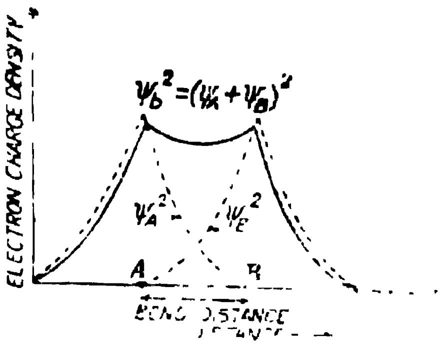


Fig 7·29—Plots of electron charge density (square of wave function) for individual atomic orbitals (dotted line) and bonding molecular orbital (solid line).

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*In an alternative system of nomenclature due to Mulliken $\sigma 2s$, $\sigma^* 2s$ $\sigma 2p$, ($\pi_y 2p$, $\pi_z 2p$), ($\pi_y{}^* 2p$ $\pi_z{}^* 2p$) and $\sigma^* 2p$ are also being denoted as $z\sigma$, $y\sigma$, $x\sigma$ ($w\pi$, $v\pi$ and $u\sigma$) respectively.

**It is assumed that the atomic orbital wave functions of two combining atoms make equal contribution to the resulting molecular orbital.

is the bond. This linear combination ($\psi_b = \psi A + \psi B$) describes a **bonding molecular orbital.**

In Fig. 7·29, the electron charge density of the bonding molecular orbital ψ_b^2 is represented by the solid line and the electron charge densities ($\psi^2 A$ and $\psi^2 B$) of the individual atoms are shown by dotted line. Points A and B in the figure present the nuclei of the two atoms. It is seen from the figure that there is more concentration of charge between the two nuclei in the case *of molecular orbital than for the individual atomic orbitals.*

Squaring Eqn. (2), we get

$$\psi_a^2 = \psi^2 A \quad 2\psi A\ \psi B + \psi^2 B \qquad \ldots(4)$$

It is seen from Eqn. (4) that charge density of the molecular orbital (ψ_a^2) is less than the sum of charge densities of the two isolated atoms ($\psi^2 A + \psi^2 B$) by the term $2\psi A\ \psi B$ This means that in this molecular orbital ***there is less charge density between the interacting atoms than there would be between the non-interacting atoms.*** The energy of this molecular orbital is, therefore, greater than the sum of the energies of the component atoms A and B, and the resultant bond is less stable. The high energy molecular orbital obtained by the linear combination ($\psi_a = \psi A - \psi B$) is termed **anti-bonding molecular** orbital.

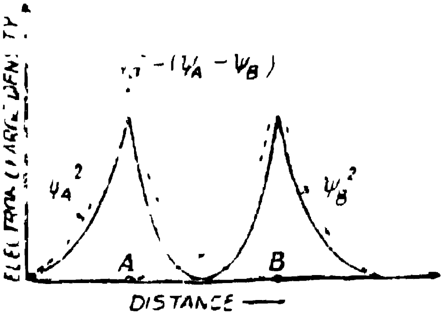

Fig 7·30—Plots of electron charge density for an antibonding orbital (solid line) and individual atomic orbitals (dotted line)

In Fig. 7·30, ψ_a^2 is shown by the solid line and the charge density of the separate atomic orbitals is represented by the dotted line. The two nuclei are represented by the points A and B. The point where the solid line touches the X-axis between the points A and B is the node point where electrons charge density is zero. This means that electrons are rarely found between the nuclei in the antibonding orbital and the nuclei repel each other.

Considering the atomic orbital as a wave having a crest (+sign) and a trough (−sign*) as shown in Fig. 7·31, we can interpret bonding and antibonding molecular orbitals in terms of and signs assigned to the interacting orbitals. If the crest of one wave overlaps the crest of other wave or trough of one overlaps the trough of the other, the new wave is reinforced. The new wave resulting from this type of *in phase overlap* is analogous to the formation of a bonding molecular orbital. We

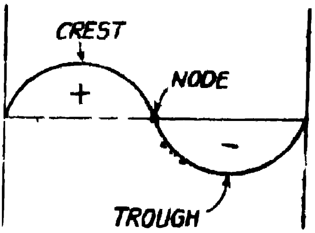

Fig. 7·31—Standing waves showing crest (+ sign) and trough (— sign).

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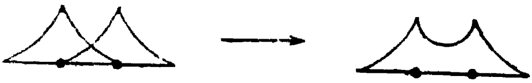
*+ and – signs are only arbitrarily assigned to crests and troughs of the wave and have nothing to do with the electrical charges

can say that *a bonding molecular orbital results from a combination of atomic orbitals with identical sign.*

Now if the crest (+ sign) of one wave overlaps the trough (— sign) of the other, the resulting wave is greatly weakened. The new wave resulting from such *out-of-phase overlap* is analogous to the formation of an antibonding molecular orbital. Thus we can say that *an antibonding molecular orbital results from an overlap of atomic orbitals with opposite signs*

Combination of *s* Orbitals. An H_2 molecule is obtained by a linear combination of two 1*s* orbitals belonging to the two hydrogen atoms. Thus combination of the two* $\psi - r$ curves (addition) of 1*s* orbitals [Fig. 7·32 (*a*)] gives an approximate $\psi - r$ curve for the molecular orbital [Fig. 7·32(*b*)].



(*a*) The $\psi - r$ curves for two 1*s* atomic orbitals of hydrogen atoms

(*b*) The $\psi - r$ curve for the $\sigma 1s$ molecular orbital for H_2 molecule obtained.

Fig. 7·32 —The $\psi - r$ curve for the $\sigma 1s$ molecular orbital of H_2 molecule formed by the combination (by addition) of two $\psi - r$ curves for 1*s* atomic orbitals of two hydrogen atoms

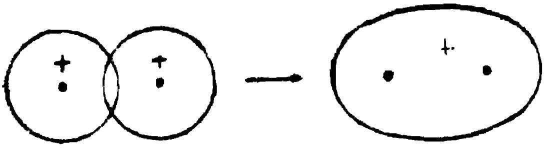


Fig. 7·33 —The boundary surface of $\sigma 1s$ molecular orbital formed from two 1*s* atomic orbitals,

In terms of charge clouds the addition of two 1*s* orbitals can be represented as shown in Fig. 7·34

There is accumulation of negative charge between the two nuclei. The accumulated charge holds the two nuclei together at the inter-nuclear distance. The molecular orbital so obtained is said to be a **bonding orbital**. Why is it named $\sigma 1s$ molecular orbital ? Notation σ is used on account of its being symmetrical

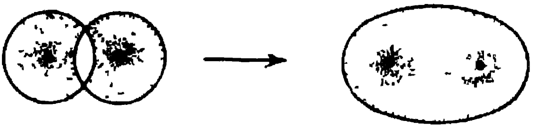
---

***Position** of a point P relative to another point O **can be** expressed in **terms of**

(*a*) **Cartesian Coordinates** *x*, *y* **and** *z* or

(*b*) **Polar Coordinates** *r*, θ **and** φ. $\psi - r$ denote variation of the wave function **with** *r*.

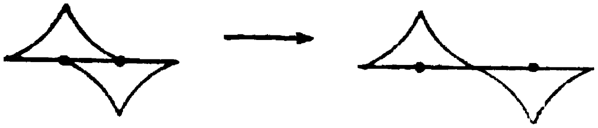
about the molecular axis and 1s is used since it is a combination of two 1s atomic orbitals.



(a) Two 1s atomic orbitals (b) Resulting σ1s molecular orbital

Fig 7·34—Charge cloud representation of the formation of σ1s molecular orbital formed from two 1s atomic orbitals.

The two 1s atomic orbitals may now be combined by subtraction. For this we may add them after changing the sign of one of these as shown in Fig. 7·31.

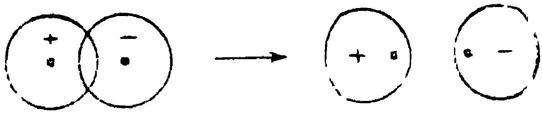


(a) The ψ—r curves for two 1s atomic orbitals after changing the sign of one of them

(b) The ψ, r curve for the σ*1s molecular orbital obtained by combination of 1s atomic orbitals by subtraction

Fig 7·35 Formation of antibonding σ*1s molecular orbital by combination of two 1s atomic orbitals by subtraction.

In terms of charge clouds combination of two 1s orbitals by subtraction can be represented as shown in Fig 7·35.



Two 1s atomic orbitals with sign of one changed

Antibonding σ*1s molecular orbital

Fig 7·36—Formation of anti-bonding σ*1s molecular orbital by combination of two 1s orbitals by subtraction shown in terms of boundary surfaces

It is seen that negative charge is withdrawn from the region between the two nuclei. As a result of it the repulsive forces between the two nuclei become stronger and its energy increases. This high energy molecular orbital is termed anti bonding orbital.

Combination of *p* Orbitals. Overlap of *p* orbitals can be either end-on (along their axes) to give σ molecular orbital or broadside on (sideways overlap) to form π-molecular orbital. Two molecular orbitals obtained by combination of two $2p_x$ atomic orbitals are :

(*i*) **Bonding orbital $\sigma 2p_x$ obtained by their addition, and**

(*ii*) **Antibonding orbital $\sigma^* 2p_x$ obtained by their subtraction.**

Sideway overlap of $2p_y$ or $2p_z$ gives rise to either bonding molecular orbital (by addition) $\pi_y 2p$ or $\pi_z 2p$ or antibonding molecular orbital (by subtraction) $\pi_y{}^* 2p$ or $\pi_z{}^* 2p$.

The electronic charge distribution of different molecular orbitals is depicted in Fig. 7·37. It is seen that in the case of bonding orbitals

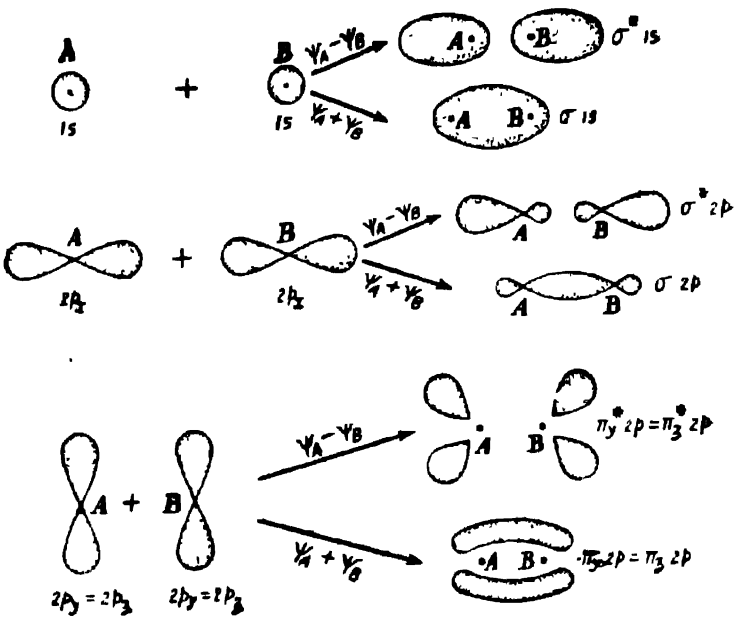


Fig. 7·37—Distribution of electronic charge density of the molecular orbitals formed from the combination of atomic orbitals.

there is a build-up of electron charge density between the nuclei. This increased electron charge density lowers the repulsion between the positive nuclei and gives rise to bonding or attractive state. In the case of anti-bonding orbitals there is only a small charge density between the nuclei and hence there is a net repulsion between the two atoms. The antibonding orbitals, therefore, do not give rise to bonding.

The order of the energy levels of these molecular orbitals which gives the order in which they fill up, is in order of increasing energy.

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p < \begin{Bmatrix} \pi_y 2p \\ \pi_z 2p \end{Bmatrix} < \begin{Bmatrix} \pi_y{}^* 2p \\ \pi_z{}^* 2p \end{Bmatrix} < \sigma^* 2p.$$

Each orbital can hold two electrons. It may be noted that $\pi_y 2p$ and $\pi_z 2p$ *bonding molecular orbitals are of equal energy, i.e., they* *are degenerate*. According to Hund's rule, these orbitals are first singly filled and pairing starts only when more electrons are to be accommodated. In a similar manner, $\pi_y{}^*2p$ and $\pi_z{}^*2p$ anti-bonding molecular orbitals are degenerate and are filled just like degenerate bonding orbitals.

Relationship between Electronic Configuration and molecular behaviour

(1) **Bond order**. We have seen that bonding electrons help in the formation of bonds whereas the anti-bonding ones oppose it. *Number of covalent bonds in the molecule (also known as bond order) is given by one-half the difference between the number of electrons in the bonding orbitals and in the anti-bonding orbitals.*

If number of electrons in the bonding orbital is N_b and those in antibonding orbitals is N_a, then

$$\text{bond order} = \tfrac{1}{2}(N_b - N_a)$$

(2) **Stability of the Molecule**. Since electrons in bonding orbitals (N_b) add to the stability of the molecule whereas those in anti-bonding orbitals (N_a) decrease its stability, stability of the molecule on the whole depends on their difference.

(*i*) The molecule is stable if $N_b > N_a$.

(*ii*) The molecule is unstable if $N_b < N_a$.

(*iii*) The molecule is unstable even when $N_b = N_a$. This is because the effect of antibonding electrons is somewhat stronger than that of the bonding electrons.

The stability of a diatomic molecule is given by dissociation energy which is proportional to its bond order.

Nitrogen is more stable than oxygen as is evident from its relative inertness towards chemical reaction as compared to oxygen*. This is because bond order in nitrogen (=3) is greater than the bond order in oxygen (=2). This trend is a general one.

(3) **Bond Order may be Integral or Fractional**. Bond order of 1, 2 or 3 corresponds to familiar single, double and triple bonds. But bond order may be fractional also.

(4) **Bond Length Related to Bond Order**. Bond length is inversely related to bond order. The higher the bond order, smaller the bond length.

(5) **Paramagnetic or Diamagnetic Character of Molecules**. A molecule having unpaired electrons is found to be paramagnetic and the one with all the electrons paired is diamagnetic.

Based on the above principles the build-up of the electron configuration of some homonuclear diatomic molecules is given below :

(*i*) **Hydrogen**. Hydrogen molecule is formed by the entry of two 1*s* electrons of the two hydrogen atoms into $\sigma 1s$ molecular orbital with paired spins. The molecular orbital configuration of H_2 is, therefore $(\sigma 1s)^2$, the superscript indicating the number of electrons in the molecular orbital. Since both the electrons are in the bonding orbital, the number of bonds $= \frac{1}{2}(N_b - N_a) = \frac{1}{2}(2-0) = 1$, *i.e.*, the two hydrogen atoms are bonded through a single covalent bond in the hydrogen molecule.

---

*The bond energies of the nitrogen and oxygen molecules are 945·6 and 497·9 kJ per mole respectively.

(*ii*) **Helium**. In the case of He_2, the four electrons, two from each helium atom, are placed in the bonding $\sigma 1s$ and anti-bonding $\sigma^* 1s$ orbitals giving the configuration $[(\sigma 1s)^2(\sigma^* 1s)^2]$. Number of bonds $= \frac{1}{2}(N_b - N_a) = \frac{1}{2}(2-2) = 0$, *i.e.*, this molecule does not exist, since bonding energy of the $\sigma 1s$ orbital is more than cancelled by the anti-bonding $\sigma^* 1s$ orbital.

(*iii*) **Nitrogen**. There are fourteen electrons in the N_2 molecule—seven from each atom $(1s^2, 2s^2, 2p^3)$. Molecular orbital configuration of the molecule is

$$KK(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p)^2(\pi_y 2p)^2(\pi_z 2p)^2$$

wherein KK denotes the closed K shell structure $(\sigma 1s)^2(\sigma^* 1s)^2$. It is assumed that these closed shells do not enter into bonding. These closed shells which do not enter into bonds are known as *non-bonding orbitals* and the electrons placed in them are called *non-bonding electrons*. A schematic representation of the formation of the molecular orbitals of N_2 is given in Fig. 7·38.

No. of covalent bonds $= \frac{1}{2}(N_b - N_a) = \frac{1}{2}(8-2) = 3$

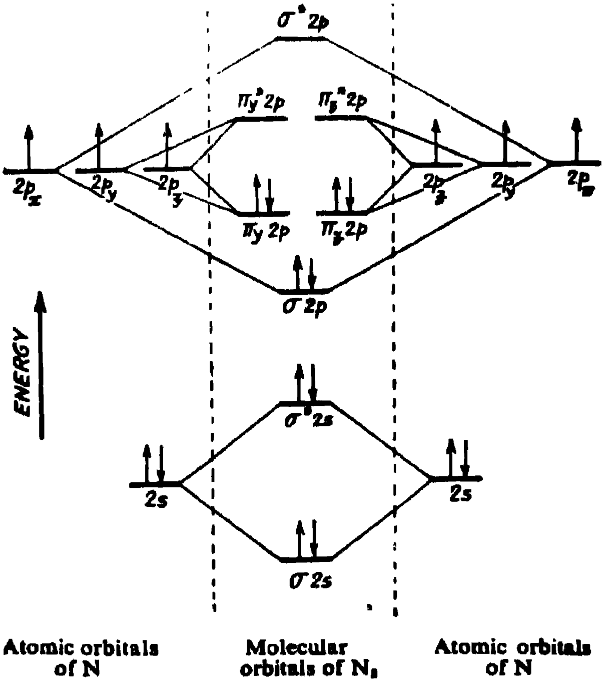


Fig. 7·38—The formation and the relative energies of the molecular orbitals in N_2.

i.e., the two nitrogen atoms are bonded through a triple covalent bond.

(*iv*) **Oxygen.** One of the greatest successes of molecular orbital theory was the relative simplicity with which it explained the paramagnetism of the oxygen molecule. The molecule of oxygen has two electrons more than N_2. These two electrons must enter the anti-bonding $\pi_y{}^*2p$ and $\pi_z{}^*2p$ orbitals filling them singly. The resulting electronic configuration of the O_2 molecule is

$$\text{KK } (\sigma 2s)^2(\sigma^*2s)^2(\sigma 2p)^2(\pi_y 2p)^2(\pi_z 2p)^2(\pi_y{}^*2p)^1(\pi_z{}^*2p)^1$$

No. of covalent bonds $=N_b-N_a=\frac{1}{2}(8-4)=2$

i.e., the two oxygen atoms are bonded through a double covalent bond. Further the two unpaired anti-bonding electrons make the molecule paramagnetic. A schematic representation of the formation of the molecular orbitals of O_2 is given in Fig. 7·39.

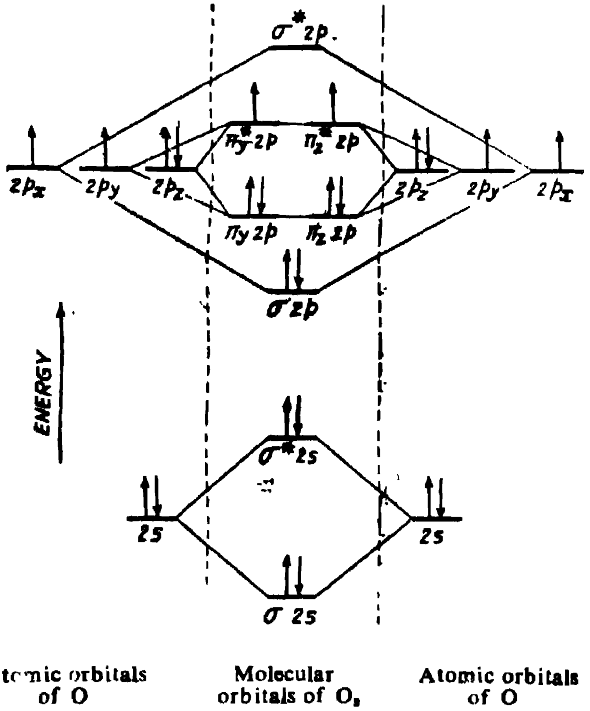


Fig. 7·39—The formation and the relative energies of the molecular orbitals in O_2.

8. Bond Lengths and Bond Energies.—A bond is formed between two atoms by overlapping of the atomic orbitals. This overlap of atomic orbitals to form molecular orbitals occurs only at certain distances between the atoms. This distance between the two nuclei is called bond distance or bond length. The bond distance between two given atoms, *e.g.*, C—H, is essentially constant in different molecules, *e.g.*, methane, ethane, propane, etc. There are, however, some exceptions to this which we shall examine later. Normal covalent bond lengths of some commoner bonds are given below :

Bond	*Distance in Å units*	*Bond*	*Distance in Å units*
C—C	1·54	C=C	1·40
C—N	1·47	C≡C	1·21
C—O	1·43	C=O	1·20
C—F	1·42	C=N	1·28
C—Cl	1·77	C≡N	1·15
C—Br	1·91	H—O	0·97
C—I	2·13	H—N	1·03
C—H	1·12	H—S	1·35

Bond Energies. There are two types of bond energy :

(*i*) Dissociation energy (designated by *D*), and

(*ii*) Bond energy (designated by *E*).

(*i*) **Dissociation energy** (*D*). It is the energy required to break a particular bond in a polyatomic molecule, in the **gaseous** state, into neutral fragments (free radicals) in the gaseous state, *i.e.*, energy required for the reaction

$$\mathrm{A{-}B}(g) \longrightarrow \underset{(\textit{Free radicals})}{\mathrm{A}^{\cdot}(g) + \mathrm{B}^{\cdot}(g)}$$

is dissociation energy, *D*.

(*ii*) **Bond energy** (*E*). In methane all the four C—H bonds are equivalent but the energy required to break the first bond ($\mathrm{CH_4} \rightarrow \mathrm{CH_3}^{\cdot} + \mathrm{H}^{\cdot}$) is not the same as the energy required to break the second bond ($\mathrm{CH_3}^{\cdot} \rightarrow :\mathrm{CH_2} + \mathrm{H}^{\cdot}$), and so on. That is, the individual dissociation energies of the four C—H bonds are different. Dissociation energy of C—H bond is found to be different in methane, ethane, propane and isobutane. This shows that dissociation energy of a bond depends on the nature of the rest of the molecule also.

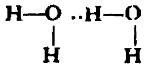
In practice, we take an average of all the different values and this *average value* is termed *bond energy*. Bond energies (kJ/mole and kcal/mole) of some commoner bonds are listed below :

Bond	*Energy*		*Bond*	*Energy*	
	kJ	(kcal)		kJ	(kcal)
$\mathrm{CH_3}$—H	426·8	102	C—N	284·5	68
$\mathrm{MeCH_2}$—H	405·8	97	C=N	615·1	147
$\mathrm{Me_2CH}$—H	393·3	94	C≡N	866·8	207
$\mathrm{Me_3C}$—H	374·5	89·5	C—F	447·7	107
C—H(av.)	414·2	99	C—Cl	326·4	78
C—C	347·3	83	C—Br	284·5	68
C=C	606·7	145	C—I	213·4	51
C≡C	803·3	192	H—H	431·0	103
C—O	334·7	80	H—N	389·1	93
C=O	694·5	166	H—O	464·4	111
C—S	272·0	65	H—F	560·7	134
N—N	163·2	39	H—Cl	426·8	102
N=N	418·4	100	H—Br	364·0	87
N≡N	945·6	226	H—I	297·1	71
O—O	146·4	35	F—F	150·6	36
O=O	497·9	119	Cl—Cl	242·7	58
S—S	225·9	54	Br—Br	188·3	45
			I—I	150·6	36

9. The Hydrogen Bond.—Compounds containing OH or NH groups often exhibit unexpected properties, *e.g.*, relatively high boiling points. To account for these abnormalities and on the basis of available evidence of many kinds, it is proposed that *when a hydrogen atom lies between two atoms having strong electronegativities, it shows a unique property of forming a bond or bridge between them, holding one by covalent bond and the other by purely electrostatic forces.* The electrostatic bond (hydrogen bond) has a strength of about 21 kJ per mole (compare with 200-400 kJ/mol for most covalent bonds). Liquids whose molecules are held together by hydrogen bonds are said to be associated and their high boiling points are due to greater energy required to break the hydrogen bonds. Hydrogen bonding between formulae is generally indicated by dotted lines. For example, in

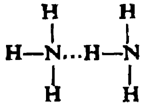
$H-F\cdots H-F$

Hydrogen fluoride
(*associated*)



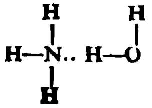
$H-\underset{\underset{H}{|}}{O}\cdots H-\underset{\underset{H}{|}}{O}$

Water
(*associated*)

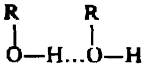


$H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N}}\cdots H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N}}$

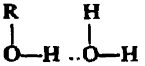
Ammonia
(*associated*)



$H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N}}\cdots H-\overset{\overset{H}{|}}{O}$



$\overset{\overset{R}{|}}{O}-H\cdots\overset{\overset{R}{|}}{O}-H$

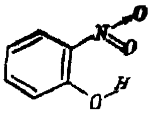


$\overset{\overset{R}{|}}{O}-H\cdots\overset{\overset{H}{|}}{O}-H$

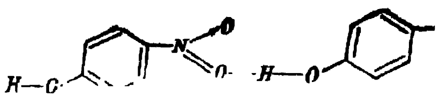
Hydrogen bonding is only a kind of specially strong dipole-dipole attraction. When hydrogen is attached to a strongly electronegative atom (*e.g.*, F, O or N), the electron cloud is strongly distorted towards the electronegative atom, exposing the hydrogen nucleus. The strong positive charge of the thinly shielded hydrogen nucleus is strongly attracted by the negative charge of the electronegative atom of the second molecule. The attraction is much weaker than the covalent bond holding it to the first electronegative atom. The electrostatic attraction is, however, much stronger than other dipole-dipole attractions.

Hydrogen bonding is important only when both electronegative atoms come from the group : F, O, N. This is because hydrogen bonded to one of these three elements only is positive enough and further only these three elements are negative enough for the necessary attraction to exist. Their special effectiveness is due to their high electronegativity coupled with their small size If the atom has a greater radius the electrostatic forces are weaker. Since the hydrogen atom has a tiny volume, the tiny charge in $H^{\delta+}$ will exert a large electrostatic attraction. On the other hand chlorine, which has the same electronegativity as nitrogen, forms very weak hydrogen bonds since its atomic radius is greater.

Hydrogen bonding affects all physio-chemical properties such as m.p., b.p., solubility, spectra, etc. For example, association results in higher boiling point. In compounds like *o*-nitraphenol hydrogen bond formation occurs *intramolecularly*, *i.e.*, involving only one molecule resulting in ring formation or chelation. Chelation results in lower boiling point, *i.e.*, greater volatility and lower solubility.



o-nitrophenol
(Intramolecular
hydrogen bonding)



p-Nitrophenol (Intermolecular
hydrogen bonding)

In *p*-nitrophenol or *m*-nitrophenol different molecules are joined through hydrogen bonding. This is termed *Intramolecular hydrogen bonding*.

Due to lower solubility and greater volatility, the o-nitrophenol can be separated from them and *p*-isomers by steam distillation.

The solubility of lower alcohols in water is due to hydrogen bonds that can exist between molecules of alcohols and molecules of water.

Hydrogen bonding is responsible for the association of molecules in water for which reason it exists as a liquid. Since it is absent in the H_2S molecules, the latter exists as a gas.

Glycerol, $CH_2OH—CHOH—CH_2OH$, is far more viscous than ethanol, C_2H_5OH. This is because glycerine having three OH groups per molecule can form many more hydrogen bonds per molecule. This increases the net attraction between all the molecules and hence increased resistance to flow.

10. Inter-molecular Forces and Physical Properties.— Various inter-molecular forces which exist in different compounds are :

(*a*) **Inter-ionic forces.** In an ionic compound the structural units are ions. For example, solid sodium chloride is made up of Na^+ ions and Cl^- ions. Each Na^+ ion is attached to six Cl^- ions surrounding it and each Cl^- ion is attached to six Na^+ ions around it. The inter-ionic forces are very powerful electrostatic forces and hold each ion in position.

(*b*) **Inter-molecular forces.** In non-ionic compounds the structural units are molecules. The forces holding these molecules together are generally very weak and are of two types as given below :

(*i*) **Dipole-dipole interaction.** In polar molecules there is an attraction between the positive end of one polar molecule and the negative end of another polar molecule, and so on. As a result of this dipole-dipole interaction, polar molecules are generally held to each other more strongly than are non-polar moelcules of comparable molecular mass.

(*ii*) **Van der Waals forces.** In non-polar compounds there is a weak intermolecular attraction due to the electrostatic attraction between the nuclei of one molecule and the electrons of the other. This electrostatic attraction is largely compensated by the electrostatic repulsion between the electrons of one molecule and the electrons of the other, as well as the repulsion of the nuclei of one by the nuclei of the other. These van der Waals forces have a very short range and become significant only when the molecules are very close together. They act only between the portions of different molecules that are in close contact, that is, between the surfaces of molecules. Larger the molecule, larger is its surface area and hence stronger the van der Waals forces. As the number of electrons in a molecule increases the van der Waals forces between the molecules increase.

The physical properties of a compound depend largely upon what kind of bonds hold its atoms together in the molecule. For example,

(*a*) **Melting point**. *Melting is the change from a highly ordered arrangement of particles in the crystalline lattice to the more random arrangement that characterises a liquid.* A solid melts when the thermal energy of its particles is large enough to overcome the interparticle forces which hold them in position.

In an ionic compound the strong inter-ionic forces are overcome only at very high temperatures and their melting points are high. In non-ionic compounds the inter-molecular forces (dipole-dipole attraction or van der Waals forces) are weak and their melting points are low.

(*b*) **Boiling point**. A liquid boils when thermal energy of the particles is enough to overcome the cohesive forces that hold them in liquid. Boiling involves breaking away of some molecules from the liquid surface.

As explained in the case of melting point, boiling points of ionic liquids are higher than those of non-ionic ones and boiling points of polar liquids are higher than those of non-polar ones.

(*c*) **Solubility**. Ionic substances are generally soluble in water due to the following reasons :

(*i*) Due to its polarity and presence of the hydroxyl group, —OH, it has a high solvating power and solvates the ion strongly.

(*ii*) Due to its high dielectric constant it lowers the attractions between oppositely charged ions once they are solvated.

In the case of non-ionic compounds, non-polar or weakly polar compounds dissolve in non-polar or weakly polar solvents and highly polar substances dissolve in highly polar solvents (useful rule of *Like dissolves like*).

11. Acids and Bases.—We have seen above how physical properties depend on inter-molecular forces. Chemical properties too depend upon molecular structure. Indeed most of this book will be concerned with finding out what this relationship is. Let us review briefly acidity and basicity, an important chemical property fundamental to the understanding of organic chemistry.

According to **Bronsted-Lowry definition**, *an acid is a substance that gives up a proton, and a base is a substance that accepts a proton.*

In a typical acid-base reaction

$$HX + B \rightleftharpoons X^- + HB^+$$

HX being a proton donor is an acid and B being a proton acceptor is a base in the forward reaction. In the back reaction HB^+ being a proton donor is an acid and X^- being a proton acceptor is a base. To make a distinction between the two acids and two bases, those on the right-hand side of the equation are referred to as the **conjugate acid** and the **conjugate base**. Thus HB^+ is a conjugate acid of the base B and X^- is a conjugate base of acid HX. $HX—X^-$ and $HB^+—B$ constitute two conjugate acid-base pairs. **The acid and base in each conjugate pair differ by a proton.** In order that an acid may exhibit its acidic properties there must be a proton acceptor (base) present. Some examples are :

$$\begin{array}{lclcccl} \textit{Acid} & & \textit{Base} & & \textit{Conjugate acid} & & \textit{Conjugate base} \\ HCl & + & H_2O & \rightleftharpoons & H_3O^+ & + & Cl^- \\ HSO_4^- & + & NH_3 & \rightleftharpoons & NH_4^+ & + & SO_4^{2-} \\ NH_4^+ & + & H_2O & \rightleftharpoons & H_3O^+ & + & NH_3 \end{array}$$

conjugate

conjugate

An acid-base reaction always proceeds in the direction of formation of the weaker acid and the weaker base.

In the equilibrium

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- \quad ..(1)$$

where HA is a strong acid, the fact that equilibrium lies far to the right implies that A^- has very little affinity for protons. Therefore, A^- must be a weak base. This observation may be generalised as follows :

The conjugate base of a strong acid is always a weak base and the conjugate base of a weak acid is always a strong base.

Strength of an acid depends on the extent of its ionisation. Hence equilibrium constant, K_a of the above reaction gives a quantitative measure of the strength of the acid. Similarly, dissociation constant, K_b of the reaction $B + H_2O \rightleftharpoons BH^+ + OH^-$ gives a quantitative measure of the strength of the base.

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \quad \text{and} \quad K_b = \frac{[BH^+][OH^-]}{[B]}$$

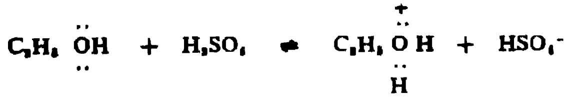
The larger the value of the equilibrium constant, K_a, the more complete the reaction (1), the higher the concentration of H_3O^+, and stronger is the acid. Similarly, the larger the value of K_b, stronger is the base.

Problem. For acetic acid, CH_3COOH, $K_a = 1·79 \times 10^{-5}$. For hydrocyanic acid, HCN, $K_a = 7·2 \times 10^{-10}$. Which is the stronger acid ?

[**Answer.** Acetic acid, with larger K_a is the stronger acid.]

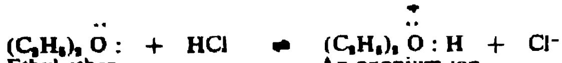
In order to avoid writing negative powers of 10, K_a is generally converted into pK_a ($pK_a = -\log_{10} K_a$). Thus while K_a for acetic acid in water at 288K is $1·79 \times 10^{-5}$, its $pK_a = -\log_{10} 1·79 \times 10^{-5} = 4·76$. *The smaller the numerical value of pK_a, the stronger is the acid to which it refers.*

A number of organic compounds containing oxygen, *e.g.*, alcohols, ethers, can accept protons and thus act as bases.



$$C_2H_5\ddot{\underset{\cdot\cdot}{O}}H + H_2SO_4 \rightleftharpoons C_2H_5\overset{+}{\underset{H}{\ddot{O}}}H + HSO_4^-$$

Ethanol — An oxonium ion (protonated ethanol)



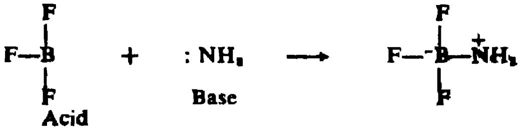
$$(C_2H_5)_2\ddot{O}: + HCl \rightleftharpoons (C_2H_5)_2\overset{+}{\ddot{O}}:H + Cl^-$$

Ethyl ether — An oxonium ion (protonated ethyl ether)

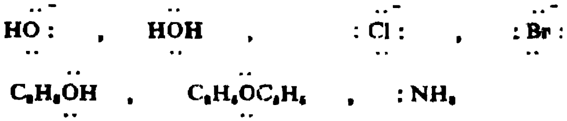
According to **Lewis definition**, *an acid is a substance that can accept an electron pair to form a covalent bond and base is a substance that can furnish an electron pair to form a covalent bond. In* other words, *an acid is an electron pair acceptor and a base is an electron pair donor*. This is the most general and fundamental of the acid-base concepts and includes all the other concepts.

A proton is an acid since it needs an electron pair to complete its shell. *It is a* **Lewis acid** *or it is an acid in the Lewis sense.* Hydroxide ion, ammonia and water are Lewis bases because they contain electron pairs available for sharing.

In reaction between BF_3 and NH_3, boron accepts the lone pair from nitrogen forming a covalent bond.



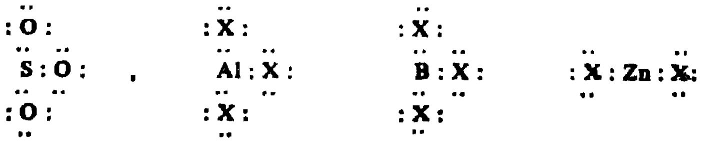
The Lewis theory does not differ from Bronsted theory with respect to substances classified as bases. A substance capable of donating an electron pair (*i.e.*, any Lewis base) is capable of donating electron pair to a proton. Being proton acceptor it is also a Bronsted base. Thus both definitions label the following species as bases.



$$H\ddot{\underset{\cdot\cdot}{O}}:^- ,\quad H\ddot{\underset{\cdot\cdot}{O}}H ,\quad :\ddot{\underset{\cdot\cdot}{Cl}}:^- ,\quad :\ddot{\underset{\cdot\cdot}{Br}}:^-$$

$$C_2H_5\ddot{\underset{\cdot\cdot}{O}}H ,\quad C_2H_5\ddot{\underset{\cdot\cdot}{O}}C_2H_5 ,\quad :NH_3$$

However, many species which are acid under Lewis definition cannot be termed so according to Bronsted definition. A few examples are sulphur trioxide and halides of boron, aluminium, iron (ferric) and zinc. The central atom in each case is able to accept a pair of electrons to complete its octet.



Similarly, a Bronsted acid like $\mathrm{H : \overset{..}{\underset{..}{Cl}} :}$, there is no vacant orbital to accept an electron pair from a base. There is, therefore, no obvious reason to label it as an acid according to Lewis definition.

Let us try to correlate the acidity and basicity with the molecular structure.

Relative Acidity of HY Molecules. To be acidic in the Bronsted-Lowry sense, the molecule must contain hydrogen which it can lose as proton. The degree of acidity will be determined by the ease with which it can lose a proton. This may be influenced by

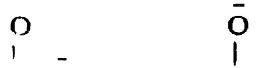
(*a*) *The strength of the Y—H bond.* The weaker the bond, the more easily it will be broken to give H^+ and stronger will be the acid. This is, however, found to be of little significance.

(*b*) *The electronegativity of Y.* The greater the electronegativity of Y, the more easily it can lose a H and the stronger the acid. Between CH_3O-H and H_3C-H, electronegativity of O being considerably greater than that of C, CH_3OH should be a stronger acid. This is actually found to be the case as is clear from their pK_a values.

$$pK_a \text{ for } CH_3OH \approx 16\ , \quad pK_a \text{ for } CH_4 \approx 50$$

(*c*) *Factors stabilising Y^- compared with HY.* Formic acid ($pK_a = 3{\cdot}77$), is comparatively a strong acid. This is partly due to the presence of an electron-withdrawing carbonyl group which enhances the electron affinity of the oxygen atom to which the incipient hydrogen atom is attached.

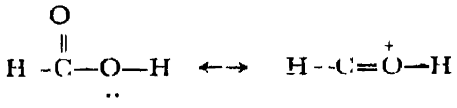
A much more important factor, however, is the stabilisation of the resultant formate ion by delocalisation.



$$\mathrm{H{-}\overset{\overset{O}{|}}{C}{-}\bar{O} \longleftrightarrow H{-}\overset{\overset{\bar{O}}{|}}{C}{=}O}$$

(*Two canonical structures of identical energy*)

There is some stabilisation in formic acid molecule itself by delocalisation. But this involves separation of charge and is, therefore, much less effective.



$$\mathrm{H{-}\overset{\overset{O}{\|}}{C}{-}\underset{..}{O}{-}H \longleftrightarrow H{-}C{=}\overset{+}{O}{-}H}$$

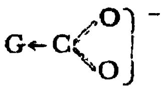
(*Two canonical structures of formic acid*)

As a result of differential stabilisation of formic acid and formate ion, equilibrium lies more towards right (formation of formate ion).

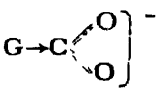
Alcohols (ROH) are weaker acids since in alkoxide ion (RO^-) obtained there is no such stabilisation by delocalisation.

Effect of Substituents on Acidity of Carboxylic Acid. Phenol is a stronger acid than alcohol, since phenoxide ion $C_6H_5O^-$ is stabilised by resonance and no such stabilisation is there in alkoxide ion. Any factor that stabilizes the anion *more than it stabilizes the acid should increase the acidity* and *any factor that makes the anion less stable should decrease acidity.*

An electron withdrawing substituent stabilises the anion by dispersing the negative charge and, therefore, increases the acidity. On the other hand electron-releasing substituents intensify the negative charge on the anion resulting in decrease of stability and thus decrease the acidity of the acid.



An electron-withdrawing substituent G withdraws electrons and stabilises the anion
(Acidity increases)



An electron-releasing substituent G releases electrons and destabilises the anion
(Acidity decreases)

For example, electron-releasing alkyl groups weaken acids, while electron-withdrawing halogens strengthen the acids. Thus

(*i*) CH_3COOH (acetic acid is about one-tenth as strong as $HCOOH$ and C_2H_5COOH (propionic acid) containing a larger alkyl group is weaker still (*Electron releasing effect of alkyl group*).

(*ii*) Chloro acetic acid ($CH_2Cl.COOH$) is 100 times as strong as acetic acid, $CHCl_2.COOH$ is still stronger and CCl_3 COOH is 10,000 times as strong as CH_3COOH (*Electron withdrawing effect of Cl atoms*)

(*iii*) Benzoic acid, C_6H_5COOH is a stronger acid than acetic acid, CH_3COOH due to the fact that $C_6H_5COO^-$ ion is better stabilised due to the presence of benzene nucleus due to which extended conjugation is possible.

In fact too many factors influence acid strength which are difficult to evaluate. This makes the reliable prediction of acid strength rather impossible. We shall, therefore, tackle the problem on the basis of only one assumption, *viz.* (*i*) *the basicity of ion is related to electron delocalisation.*

(*i*) The *greater the electron delocalisation* for a given series of basic ions, the *larger the volume over which the electron is delocalised* and the *smaller the electron density* (charge/volume).

(*ii*) The *smaller the electron density*, the *smaller the attraction for a proton* and the *weaker is the base.*

(*iii*) *The weaker the base, the stronger is its conjugate acid.*

Example 1. *Arrange the following in the order of increasing acidity :*

CH_4, NH_3, H_2O and HF

To predict their relative acidities we shall evaluate the relative basicities of their conjugate bases CH_3^- (methide ion), NH_2^- (amide ion), OH^- (hydroxide ion) and F^- (fluoride ion) respectively.

Although size of the atom decreases from C to F, volume available to electron increases from C to F. This is because in CH_3^-

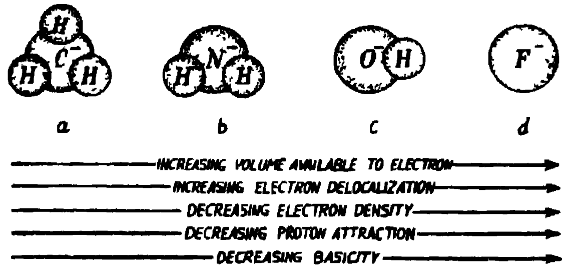

H
C⁻
H
H
N⁻
H
H
O⁻
H
F⁻
a
b
c
d
INCREASING VOLUME AVAILABLE TO ELECTRON
INCREASING ELECTRON DELOCALIZATION
DECREASING ELECTRON DENSITY
DECREASING PROTON ATTRACTION
DECREASING BASICITY

Fig. 7·40.

three-fourths of the volume of carbon atom carrying negative charge is overlapped by 3 hydrogen atoms, as illustrated in (*a*) above (Fig. 7·40). Thus, the negative charge on carbon exists over approximately one-fourth the volume of the carbon atom. Similarly, about two-thirds the volume of nitrogen carrying negative charge in NH_2^- ion is overlapped by 2 hydrogen atoms and the negative charge on nitrogen exists, therefore, over approximately one-third of its volume. Similarly, there being one hydrogen atom overlapping oxygen atom in OH^- and none overlapping fluorine atom in F^- ion, more volume is available to electron.

Thus we find that as we pass from CH_3^- to NH_2^- to OH^- to F^-, the volume available to the electron increases resulting in an increase in electron delocalisation.

As the electron delocalisation increases, the electron density decreases from (*a*) to (*d*) smaller the electron density, smaller the attraction for a proton and smaller the basicity. Hence with increase in electron delocalisation from (*a*) to (*d*), the electron density decreases and the proton attraction decreases. This means basicity decreases from (*a*) to (*d*).

As the basicity decreases from CH_3^- to F^-, the acidity of their conjugate acids increases from CH_4 to HF.

Hence arranging them in the order of increasing acid strength, we get

$$CH_4 < NH_3 < H_2O < HF$$

Example 2. *Arrange the following acids in the order of their increasing acidity :*

HF, HCl, HBr and HI

To predict their relative acidities, we shall evaluate the relative basicities of their conjugate bases F^-, Cl^-, Br^- and I^- respectively.

Here the volume of ion increases from F^- to I^-, *i.e.*, the volume available to electron increases from F^- to I^-. As a result of it electron delocalisation increases and electron density decreases from F^- to I^-; consequently the attraction for a proton decreases and basicity decreases in the order :

$$F^- > Cl^- > Br^- > I^-$$

This makes F^- as the strongest base and its conjugate acid HF as the weakest acid., Similarly I^- is the weakest base and its conjugate acid HI is the strongest acid of the series.

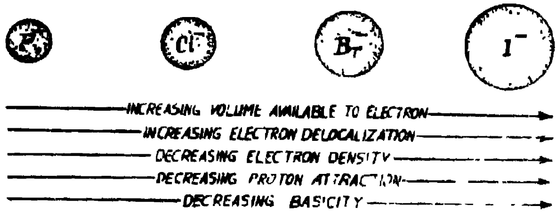

F⁻
Cl⁻
Br⁻
I⁻
INCREASING VOLUME AVAILABLE TO ELECTRON
INCREASING ELECTRON DELOCALIZATION
DECREASING ELECTRON DENSITY
DECREASING PROTON ATTRACTION
DECREASING BASICITY

Fig. 7·41

∴ Arranging them in the order of increasing acidity, we get

$$HF < HCl < HBr < HI$$

Thus in general, the acidity of binary acids increases on proceeding down a given group and across a given period from left to right in the periodic table.

Increasing acidity →

CH_4	NH_3	H_2O	HF	Increasing acidity ↓
		H_2S	HCl	
		H_2Se	HBr	
			HI	

If electronegativity alone determined the acidities of halogen acids, HF would be the strongest acid, since electronegativity of fluorine is the highest.

Strength of H—F bond is almost twice that of H—I bond. So H—I bond can be more conveniently broken to liberate a proton, with the result that HI is a stronger acid as compared to HF.

So we find that the effect of electron delocalisation as explained above and bond strength overshadows the effect of electronegativity.

Relative strengths of some acids and their conjugate bases are given in a chart (Table 7·1) for ready reference.

Relative Acidity of HOY Molecules

In compounds of the type HOY the hydrogen is present on oxygen in each case, as the variation of acidity can only be due to variations in the nature of Y. These variations must be transmitted to the O—H bond in some way, so that its effect could be felt in the acidity of the molecule

If Y is a strongly electron-withdrawing group, it will attract the electron pair shared between O and Y. This will give some positive charge to O which will attract the electron pair shared between O and H. Hydrogen will thus get a partial positive character and *the compound HOY will be more acidic. This mode of transmission of an electrical effect from atom to atom in a chain is termed* **inductive effect** (*see Sec. 12 below*).

$$\overset{\delta+}{H} \rightarrow O \rightarrow \overset{\delta-}{Y}$$

Electron-withdrawing Y increases acidity.

Table 7·1—Acid-Base Chart

(Arranged in the order of decreasing acid strength)

Acid		**Conjugate Base**	
Name	*Formula*	*Formula*	*Name*
Perchloric acid	$HClO_4$	ClO_4^-	Perchlorate ion
Sulphuric acid	H_2SO_4	HSO_4^-	Hydrogen sulphate ion
Hydrogen chloride	HCl	Cl^-	Chloride ion
Nitric acid	HNO_3	NO_3^-	Nitrate ion
Hydronium ion	H_3O^+	H_2O	Water
Hydrogen sulphate ion	HSO_4^-	SO_4^{2-}	Sulphate ion
Phosphoric acid	H_3PO_4	$H_2PO_4^-$	Dihydrogen phosphate ion
Acetic acid	CH_3COOH	CH_3COO^-	Acetate ion
Carbonic acid	H_2CO_3	HCO_3^-	Hydrogen carbonate ion
Hydrogen sulphide	H_2S	HS^-	Hydrosulphide ion
Ammonium ion	NH_4^+	NH_3	Ammonia
Hydrogen cyanide	HCN	CN^-	Cyanide ion
Phenol	C_6H_5OH	C_6H_5O	Phenoxide ion
Water	H_2O	OH	Hydroxide ion
Ethanol	C_2H_5OH	$C_2H_5O^-$	Ethoxide ion
Ammonia	NH_3	NH_2^-	Amide ion
Methylamine	CH_3NH_2	CH_3NH	Methylamide ion
Hydrogen	H_2	H^-	Hydride ion
Methane	CH_4	CH_3^-	Methide ion

If Y is an electron-releasing atom or group, the electron density around oxygen will increase. As a result of it the electron pair of H—O bond is nearly equally shared, making the compound H—O—Y a weaker acid

$$H \leftarrow \overset{\delta}{O} \leftarrow \overset{\delta+}{Y}$$

Electron-releasing Y decreases acidity.

Inductive effect of Y is always compared with that of H in H—O—H. *If* Y *is more electronegative than* H, YOH *will be stronger acid than water and if* Y *is less electronegative than* H, YOH *will be weaker acid than water.*

For example, in NaOH sodium atom is less electronegative (more electropositive) than hydrogen, so NaOH is an extremely weak acid. In HOCl, since chlorine is more electronegative than hydrogen, it is a stronger acid than water.

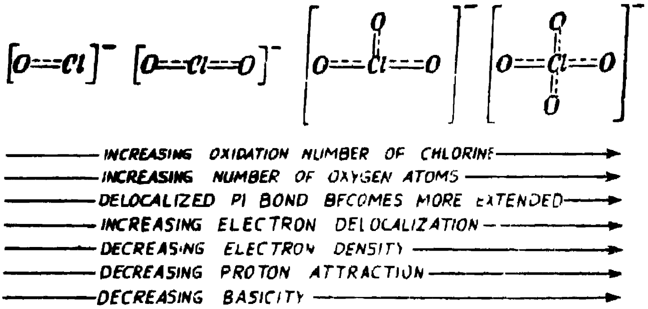
For oxyacids containing the central atom, the acidity increases with increasing oxidation number of this atom. For example, in oxyacids of chlorine acidity increases from HClO to $HClO_4$.

INCREASING ACIDITY ↓

ACID	FORMULA	OXIDATION NUMBER OF CHLORINE
HYPOCHLOROUS	$HClO$	+1
CHLOROUS	$HClO_2$	+3
CHLORIC	$HClO_3$	+5
PERCHLORIC	$HClO_4$	+7

In this case also, a reasonable explanation can be offered in terms of electron delocalisation resulting from the delocalised pi (π) bonding which embraces the chlorine and oxygen atoms in their conjugate bases ClO^-, ClO_2^-, ClO_3^- and ClO_4^-.

As the number of oxygen atoms increases, the delocalised π bond embraces more and more of oxygen atoms, *i.e.*, the delocalisation becomes more and more extended. This results in decrease in electron density and consequent decrease in proton attraction and decrease in basicity.


INCREASING OXIDATION NUMBER OF CHLORINE
INCREASING NUMBER OF OXYGEN ATOMS
DELOCALIZED PI BOND BECOMES MORE EXTENDED
INCREASING ELECTRON DELOCALIZATION
DECREASING ELECTRON DENSITY
DECREASING PROTON ATTRACTION
DECREASING BASICITY

Hence basic strength of these conjugate bases is

$$ClO^- > ClO_2^- > ClO_3^- > ClO_4^-$$

ClO^- being the strongest base, its conjugate acid, HClO will be the weakest acid. Similarly, ClO_4^- being the weakest base, its conjugate acid, $HClO_4$ will be the strongest acid. Hence arranging them in the order of increasing acidity, we get

$$HClO < HClO_2 < HClO_3 < HClO_4$$

Problem. Consider the following oxyacids of nitrogen :

HNO_3 (nitric) ; HNO_2 (nitrous) and HNO (hyponitrous)

(*a*) Calculate the oxidation number of nitrogen in each.

(*b*) Predict which acid will be the weakest and which one the strongest. Give reasons for your selection.

ELECTRON DISPLACEMENTS IN A MOLECULE

12. Inductive Effect.—Consider a chain of carbon atoms with a chlorine atom joined to the end carbon atom.

$$-C_3-C_2-C_1-Cl$$

In this chlorine atom has greater electronegativity than the carbon atom. Due to greater electronegativity Cl atom pulls the electron pair shared between C_1 and Cl towards itself. As a result of it chlorine atom acquires a small negative charge and C_1 acquires a small positive charge.

$$-C_3-C_2-\overset{+\delta}{C_1}-\overset{-\delta}{Cl}$$

As C_1 is positively charged, it attracts towards itself the electron pair shared between C_1 and C_2. This causes C_2 to acquire a small positive charge but the charge is smaller than the charge on C_1 which is now almost neutralized.

$$-C_3-\overset{+\delta}{C_2}-C_1-\overset{-\delta}{Cl}$$

Similarly, C_3 acquires a positive charge which is less than that on C_2. *This type of electron displacement along a carbon chain is termed Inductive effect.* Inductive effect is permanent and decreases rapidly as the distance from Cl (source) increases. For practical purposes the inductive effect is ignored after the second carbon atom.

It must, however, be borne in mind that the electron pairs, although permanently displaced, do not leave their valency shells. The inductive effect may be represented in a number of ways. In this book it will be represented as follows :

For measurement of relative inductive effects, atoms or groups having greater electron affinity than hydrogen are said to have $-I$ effect (electron-attracting). Similarly, atoms or groups having smaller electron affinity than hydrogen are said to have $+I$ effect (electron-repelling). Some of the groups in the order of decreasing inductive effects are :

NO_2, F, Cl, Br, I, OCH_3, C_6H_5, H
Groups having $-I$ effect

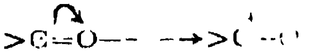
H, CH_3, C_2H_5, $(CH_3)_2CH$, $(CH_3)_3C$
Groups having $+I$ effect

This terminology ($+I$ and $-I$) is due to Ingold, while Robinson has suggested opposite signs. To avoid confusion, we shall use Ingold's terminology throughout.

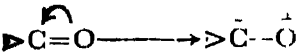
13. Electromeric Effect —In some reactions one of the two or three shared pairs of electrons between two atoms (joined by double or triple bond) is completely transferred to one of these atoms. This is a temporary effect brought into play at the requirement of the attacking reagent and takes place instantaneously. It is termed electromeric effect.

For example, in $>C=O$ or $>C\ {}^{\times}_{\times}\ .\dot{O}.$ one of the two shared pairs of electrons is completely transferred to oxygen and the electronic stucture becomes $>\overset{+}{C}\ {}^{\times}_{\times}\ \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:$, *i.e.*, carbon atom loses a share in the transferred pair of electrons and oxygen gains a share. As a result of it, carbon acquires a positive charge and oxygen acquires a negative charge. The molecule will, however, revert back to its original electronic condition when the attacking reagent is removed.

The electromeric effect is represented by means of a curved arrow beginning at the original position of the electron pair and ending where the pair has migrated. For example, the above transfer of electron pair in $>C=O$ is indicated as follows :



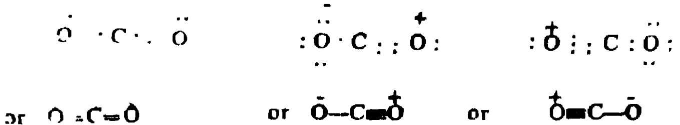
Transference of one electron pair to carbon



is most unlikely in view of the fact that oxygen is strongly electron-attracting and will oppose the electron transfer away from

In cases where both inductive and electromeric effects occur together these may be aiding or opposing each other. In the latter case, the electromeric effect generally overcomes the inductive effect. In the above example of >C=O, the effects are assisting each other.

14. Resonance.—Occasionally no reasonable electronic picture can be drawn for a molecule which could satisfactorily account for its observed properties. For example, the electronic structure of carbon dioxide may be represented by at least three possible electronic arrangements given below :



(I) (II) (III)

The calculated heat of formation of carbon dioxide for one formula is 1464 kJ mol^{-1} and the O—O distance should be 2·40 Å. However, the observed heat of formation is 1590 kJ mol^{-1} and the O—O distance is 2·30Å indicating that none of these structures satisfactorily accounts for its observed properties. This led to the idea that such compounds exist in a state which is some combination of two or more electronic structures each one of which makes some contribution to its structure.

When several structures may be assumed to contribute to the true structure of a molecule, but no one of them can be said to represent it uniquely, the molecule is referred to as a **resonance hybrid** *and the phenomenon is termed as* **resonance.**

The word resonance for this situation should not give us an impression that the molecule resonates from one structure to the other and the electron pair jumps back and forth from one bond to the other. This is totally wrong and the molecule has only one real electron structure which cannot be physically described. Thus the difficulty lies in the description and not in the molecule itself.

It is hoped that the following crude analogy will help the reader to grasp the concept of resonance. The mule is a hybrid of the jack ass and the mare. It has inherited characteristics from both the parents. For example, it can carry load like an ass and run fast like a mare. However, when we look at the mule, we do not see a jack ass at one glance and mare at another glance. We see a mule always. In a similar manner a resonance hybrid does not oscillate between its canonical structures. Its properties are fixed and these are the properties of the actual hybrid structure.

Chief conditions of resonance :

(*i*) The arrangement of the atoms must be identical or almost so in every formula.

(*ii*) The energy content of all the canonical forms must be nearly the same.

(*iii*) Each canonical form must have the same number (including zero) of unpaired electrons.

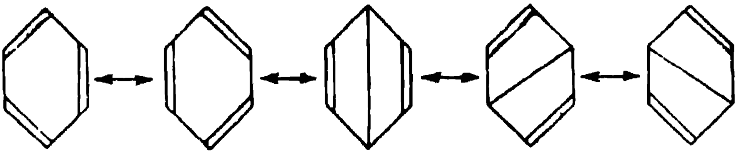
Criteria of Resonance

(*i*) *Heat of formation of a resonance hybrid is abnormally high.* The observed heat of formation of carbon dioxide (=1590 kJ mol^{-1}) is greater than the calculated value (=1464 kJ mol^{-1}). The difference (=126 kJ/mol^{-1}) is called the **resonance energy** of carbon dioxide, *i.e.*, the energy lost when a molecule of carbon dioxide takes resonance hybrid formula described earlier.

(*ii*) *Shortening of bond length.* In a resonance hybrid the bond length is smaller than in canonical structures.

(*iii*) *Stabilisation.* Greater the resonance energy, smaller the internal energy of the resonance hybrid and greater the stability. That is why a system always stabilises itself as a result of resonance

The phenomenon of resonance is also noticed in organic compounds. Thus benzene may be represented by the following structures :


(*i*) (*ii*) (*iii*) (*iv*) (*v*)

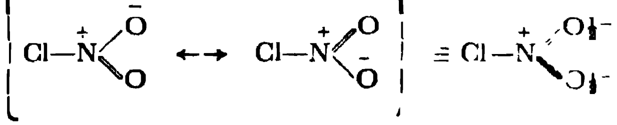
The energy of benzene is less by about 150 kJ mol^{-1} than the energy of any of its contributing forms given above. This shows that the actual state is a hybrid intermediate between all these possible forms so that the ring is not formed by alternate double and single bonds but six equivalent bonds.

A resonance hybrid is being represented in a number of ways. In this book it will be represented by putting double headed arrows between various canonical structures as shown below for carbon dioxide :

$$O{=}C{=}O \longleftrightarrow \overset{-}{O}{-}C{\equiv}\overset{+}{O} \longleftrightarrow \overset{+}{O}{\equiv}C{-}\overset{-}{O}$$

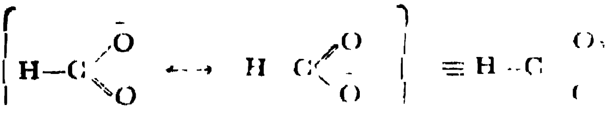
A few more examples of resonance hybrids are :

(*i*) *Nitryl chloride, NO_2Cl.*



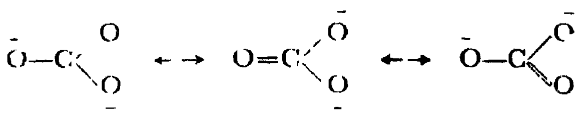
Each N—O bond is halfway between single and double, it is said to have a bond order of $1\frac{1}{2}$ and frequently written with dotted lines to represent partial bonds.

(*ii*) *Formate ion, $HCOO^-$.*



Both C—O bonds have a bond order of 1½. Accordingly C—O bond distance (=1·26Å) is between C=O double bond distance (=1·20Å) in $H_2C=O$ and C—O single bond distance (=1·43Å) in HO—CH_3.

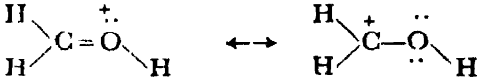
(iii) *Carbonate ion,* CO_3^{2-}.



The resonance hybrid has three equivalent C—O bonds each having a bond order of 1⅓. It has, therefore, a more single bond character than those in formate ion (bond order 1½) and is slightly longer (=1·28Å).

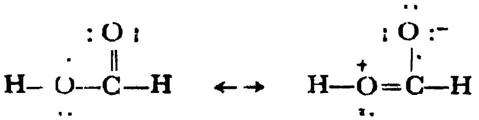
Relative importance of resonance structures for a molecule or ion can be assessed with the help of the following empirical rules :

(1) Structures in which the second row of elements (Li to F) have filled octets are more important than structures having unfilled octets. However, the non-octet structures also contribute to the resonance hybrid and this contribution increases as the difference in electronegativity between atoms increases. For example,



(More important) *(Less important)*

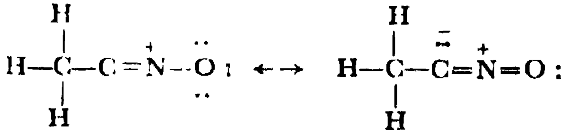
(2) Structures involving a minimum of charge separation are more important.



$$H-\ddot{O}-\overset{\overset{:O:}{\|}}{C}-H \longleftrightarrow H-\overset{+}{O}=\overset{\overset{:O:^-}{|}}{C}-H$$

(More important) *(Less important)*

In case there is charge separation in both the alternative structures, the more important structure is the one in which the negative charge is borne by the more electronegative element and the positive charge by the more electropositive element. For example, in acetonitrile oxide structure.



$$H-\underset{H}{\overset{H}{C}}-C=\overset{+}{N}-\ddot{O}: \longleftrightarrow H-\underset{H}{\overset{H}{C}}-\overset{-}{C}=\overset{+}{N}=O:$$

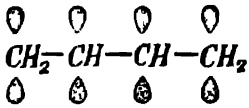
(More important) *(Less important)*

Inductive and resonance effects, which occur permanently in real molecules, are collectively known as **polarization effects.**

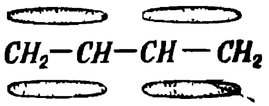
15. Delocalisation.—Compounds containing one double bond are termed alkenes and those containing two double bonds are called alkadienes. Alkadienes give usual reactions of hydrocarbons containing two double bonds. Properties of alkadienes containing

double and single bonds (conjugated systems) are abnormal. For example, these undergo abnormal addition reactions and readily polymerise.

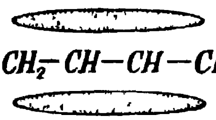
The abnormal behaviour of conjugated alkadienes is due to delocalisation of π electrons. For example, in buta-1 : 3-diene there are four *p* atomic orbitals, one of each of the four carbon atoms (**I**). Overlapping of the *p* atomic orbitals on adjacent carbon atoms gives two localised π bonds (**II**). Interaction is also possible between the *p* atomic orbitals of the two central carbon atoms, as well as each of these and the *p* orbitals on the outside carbon atoms. An alternative formulation is thus a π orbital covering all the four carbon atoms (**III**) in which the electrons are said to be ***delocalised*** as they are now spread over and held in common by all the four carbon atoms. There are, of course, two such delocalised orbitals each containing two electrons, one above and the other below the plane of the rest of the molecule.



I



II



III

$CH_2{=}CH{-}CH{=}CH_2$

IV

A support for the formula (**III**) is obtained from the fact that C=C bond lengths in (**IV**) are longer than those in ethylene while the C—C distance is slightly shorter than that in ethane. This indicates a partial single bond character of the C=C bond and a partial double bond character of the C—C bond as demanded by (**III**).

16. Hyperconjugation.—It is shown by heat of hydrogenation data that alkenes are stabilized not only by conjugation but also by the presence of alkyl groups : (*the greater the number of alkyl groups attached to the doubly-bonded carbon atom, the more stable the alkene.*) For example, propylene is more stable than ethylene.

Stabilization by alkyl group has been attributed to delocalization of electrons as in butadiene (see above), through over-

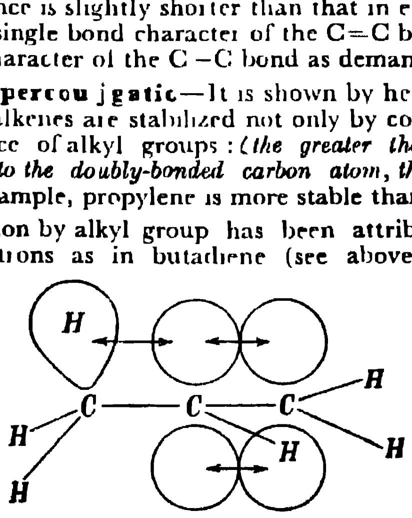
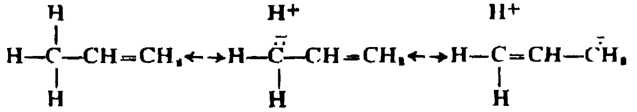


Fig. 7·42—Hyperconjugation in propylene.

lapping between a p orbital and a σ (sigma) bond orbital of the alkyl group. Because of this overlapping each pair of electrons helps bind together all the four atoms (of $C=C$ and $C—H$ groups). ***Delocalization of this kind, involving σ bond orbital, is called hyperconjugation.***

There are various ways of looking at this. The one widely used is to regard the H—C bond possessing a partial ionic character due to resonance. For example, propylene may be considered a resonance hybrid as given below :



$$H-\overset{H}{\underset{H}{C}}-CH=CH_2 \longleftrightarrow H-\overset{H^+}{\underset{H}{\bar{C}}}-CH=CH_2 \longleftrightarrow H-\overset{H^+}{\underset{H}{C}}=CH-\bar{C}H_2$$

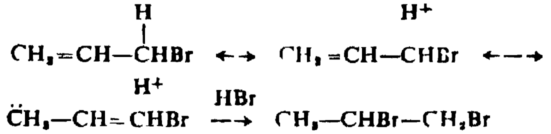
Hyperconjugation is thus no bond resonance. Its effect is to increase the ionic character of the C—H bond and partial delocalization of its electrons.

As a result of hyperconjugation in

$$\overset{1}{C}H_3-\overset{2}{C}H=\overset{3}{C}H_2 \qquad \text{(propylene)}$$

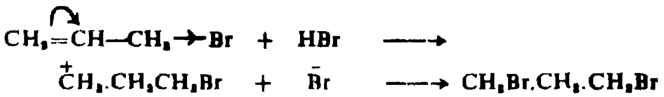
C—H bond is something less than a single bond, $C_1—C_2$ bond has some double bond character and $C_2—C_3$ bond has some single bond character. This is borne out by their bond lengths. Here C—C bond length is 1·50Å in comparison with 1·54Å for a purely single bond.

Formation of 1, 2-dibromide on addition of HBr to allyl bromide by polar mechanism, can be explained in terms of hyperconjugation.



$$CH_2=CH-\overset{H}{C}HBr \longleftrightarrow CH_2=CH-\overset{H^+}{C}HBr \longleftrightarrow \ddot{C}H_2-\overset{H^+}{C}H=CHBr \xrightarrow{HBr} CH_2-CHBr-CH_2Br$$

The inductive effect of bromine atom would tend to give 1, 3-dibromide



$$CH_2=CH-CH_2 \rightarrow Br + HBr \longrightarrow$$
$$\overset{+}{C}H_2.CH_2CH_2Br + \bar{Br} \longrightarrow CH_2Br.CH_2.CH_2Br$$

But this —I effect of bromine atom being weaker than the hyperconjugative effect, 1, 2-dibromide is formed.

In the case of allyl alcohol, —I effect of the OH group is stronger than hyperconjugation and is, therefore, the deciding factor for addition of HBr.

TEST YOUR UNDERSTANDING

1. Indicate the maximum number of electrons in a given atom which can occupy each of the following :

(*a*) The *L* shell (*b*) The $n=3$ shell (*c*) The $2p$ orbitals

(*d*) The $2p_x$ orbital (*e*) The $3d$ orbitals (*f*) The $4f$ orbitals

(*g*) The $2d$ orbitals.

2. Name the type of orbital used for bonding in the central atom of each of the following and predict the geometrical configuration for each

(*a*) NH_3 (*b*) CH_4 (*c*) NH_4^+ (*d*) H_2O (*e*) H_2S (*f*) BF_3

3. Which of the following hypothetical structures of CCl_4 will have a zero dipole moment ?

(*a*) Carbon at the centre of a square with a chlorine at each corner.

(*b*) Carbon at the apex of a pyramid and a chlorine atom at each corner of a square base.

4. The order of bond lengths in the halogen acids is: $HF < HCl < HBr < HI$; the order of their dipole moments is : $HF > HCl > HBr > HI$. Offer an explanation.

5. C—O and B—F bonds are known to be polar. How will you account for the zero dipole moment of CO_2 and BF_3 ?

6. Predict the relative acidity of—

(*a*) methanol (CH_3OH) and methylamine (CH_3NH_2)

(*b*) methanol and methanethiol (CH_3SH)

(*c*) H_3O^+ and NH_4^+.

7. Which is the stronger acid of each pair :

(*a*) H_3O^+ or H_2O (*b*) NH_4^+ or NH_3

(*c*) H_2S or HS^- (*d*) H_2O or OH^- ?

(*e*) What relationship is there between *charge* and *acidity* ?

8. Arrange the members in the following groups in the order of decreasing basicity :

(*a*) F^-, OH^-, NH_2^-, CH_3^- (*b*) HF, H_2O, NH_3

(*c*) OH^-, SH^-, SeH^- (*d*) F^-, Cl^-, Br^-, I^-,

(*e*) H_2S, HS^-, S^{-2} ; (*f*) H_3O^+, H_2O, OH^-

(*g*) NH_3, NH_2^- (*h*) CH_3OH, CH_3NH_2, CH_3F.

(*i*) What relationship is there between *charge* and *basicity* ?

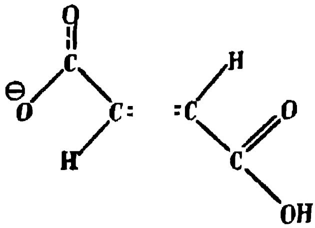
9 What is Bronsted-Lowry acid in :

(*a*) HCl dissolved in water.

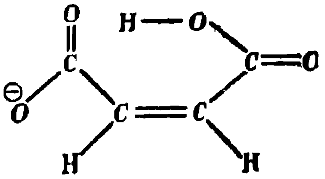
(*b*) HCl (unionized) dissolved in benzene ?

(*c*) Which solution is more strongly acidic ?

10. In which of the following ions, the carboxyl group will lose a proton more readily ? Suggest why.



A (*trans variety*)



B (*cis variety*)

11. Which of the following anions would be formed preferentially when H—O—CH_2—H (methanol) loses a proton ?

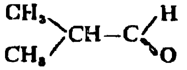
$$\overset{\ominus}{:\underset{\cdot\cdot}{O}}-CH_2-H \quad \text{or} \quad H-O-\overset{\ominus}{C}H_2$$

(A) (B)

12. What happens when $CH_3\overset{\oplus}{N}H_3$ is added to water ?

13. Write resonance hybrid structures for the following ions :

(*i*) $^{\ominus}CH_2OH$, (*ii*) $NO_2^{\ominus}$, (*iii*) $RN_2^{\oplus}$. (*iv*) $CH_2=CH-CH_2$

14.  loses a proton to form the most stable anion.

Predict, giving reasons, which proton has been lost.

KEY

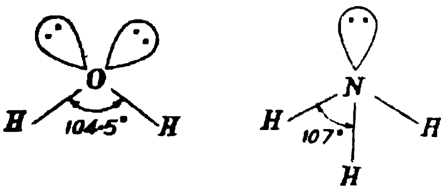
1. (*a*) 8 (*b*) 18 (*c*) 6 (*d*) 2 (*e*) 10 (*f*) 14 (*g*) 0

2. (*a*) sp^3 ; tetrahedral ; (*b*) sp^3 ; tetrahedral ;
(*c*) sp^3 ; tetrahedral ; (*d*) sp^3 ; tetrahedral ;
(*e*) p ; about 90° ; (*f*) sp^3 ; tetrahedral.

Notes. (*i*) The H—N—H bond angles in NH_3 are 107°, slightly smaller than the predicted va [illegible] It has been explained by assuming electrostatic repulsion between electron pairs in the valency shell (both bonding and lone pairs) and are in the following order :

Lone pair-lone pair > lone pair-bond pair > bond pair-bond pair

This is because lone pairs are more concentrated than bonding pairs which are stretched in the formation of covalent bonds. Thus the lone pair in ammonia exerts greater electrostatic repulsion on the three bonding pairs which are 'forced together'. The bond angle, therefore, decreases from 109·5° to 107°.



Water Ammonia

Fig. 7·39—Bond angles in water and ammonia.

(*ii*) In water H—O—H angle is 104·5°, smaller than the calculated tetrahedral angle, and even smaller than the angle in NH_3. Here there are two unshared pairs of electrons compressing the two bonding pairs which are 'closed up' more than in ammonia.

3. Structure (*a*) not (*b*)

4. $\mu = e \times d$. The value of e is determined by the electronegativity of X the order of which is F(4·0)>Cl(3·0) Br(2·8)>I(2·5). Here e increases more rapidly from I to F than decrease of d from HI to HF. Hence the product $e \times d$ increases from HI to HF.

5. CO_2 linear ; BF_3 flat, trigonal.

6. (*a*) $CH_3OH > CH_3NH_2$; (*b*) $CH_3SH > CH_3OH$;
(*c*) $H_3O^+ > NH_4^+$.

7. (*a*) H_3O^+ ; (*b*) NH_4^+ (*c*) H_2S ; (*d*) H_2O.

8. (*a*) $CH_3^- > NH_2^- > OH^- > F^-$; (*b*) $NH_3 > H_2O > HF$;
(*c*) $OH^- > SH^- > SeH^-$; (*d*) $F^- > Cl^- > Br^- > I^-$;
(*e*) $S^{2-} > HS^- > H_2S$; (*f*) $OH^- > H_2O > H_3O^+$;
(*g*) $NH_2^- > NH_3$; (*h*) $CH_3NH_2 > CH_3OH > CH_3F$

9. (*a*) H_3O^+ ; (*b*) HCl ; (*c*) HCl in benzene.

10. In A because the *cis* variety B is stabilised by intramolecular hydrogen bonding beetween O of the C=O group and H of the H—O part of the COOH group. Extra energy is, therefore, required for removal of a proton from B.

11. Anion A will be formed preferentially since it is more stable due to negative charge being present on a more electronegative atom.

12. Following equilibrium is set up

$$CH_3\overset{\oplus}{N}H_3 + H_2O \rightleftharpoons CH_3NH_2 + H_3O^{\oplus}$$

Nitrogen being less electronegative than oxygen, a positive charge on nitrogen is preferred to a positive charge on oxygen. Proton will, therefore, be mostly attached to amine rather than water, *i.e.*, equilibrium constant will be small.

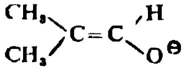
13. (*i*) $H_2\overset{\oplus}{C}—O—H \leftrightarrow H_2C=\overset{(+)}{O}—H$

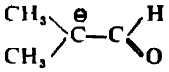
(*ii*) $\overset{\ominus}{O}—N=O \leftrightarrow O=N—\overset{\ominus}{O}$

(*iii*) $R—\overset{\oplus}{N}\equiv N \leftrightarrow R—N=\overset{\oplus}{\ddot{N}}$

(*iv*) $H_2C=CH—\overset{\oplus}{C}H_2 \leftrightarrow H_2\overset{(+)}{C}—CH=CH_2$

14. Proton on the carbon atom next to the carbonyl group is lost, since the resultant anion, being stabilised by delocalisation, is more stable than either of the alternative ions.





QUESTIONS

Essay Type :

1. Distinguish between shells, subshells and orbitals. State rules of distribution of electrons into various shells, subshells and orbitals.

2. Write explanatory notes on the following :

(*i*) ionization potential, (*ii*) electron affinity, and (*iii*) electronegativity. (*Delhi B.Sc. 1976 Supp.*)

3. Study carefully the table given below and answer the following questions :

Substance	M.P. (K)	B.P. (K)
(1) Helium	3·3	4·1
(2) Methane	89	111
(3) Carbon dioxide	—	sublimes at 194·5
(4) Carbon tetrachloride	250	349·8
(5) Water	73	373
(6) Sodium chloride	1073·4	1686
(7) Silica	about 2000	about 2500
(8) Diamond	about 3800	about 4500

(*a*) In which of these substances does hydrogen bonding occur ?

(*b*) In which of these intermolecular attraction is mainly due to van der Waals forces ?

(*c*) Which of them forms a molecular solid made up of polar molecules ?

(*d*) In which of the solid substances do the weakest bonds exist ?

(*e*) Which of the solid substances is an ionic compound ?

(*f*) How can you explain the differences in melting and boiling points between carbon dioxide and silica ?

4 Explain why—

(*a*) Glycerine is far more viscous than ethanol

(*b*) Hydrogen sulphide is a gas whereas water is a liquid

(*c*) Methanol is quite soluble in water while carbon tetrachloride is insoluble in it

5 The dipole moments of some molecules are given below :

Ammonia = 1.46D , Carbon dioxide = zero , Methyl chloride = 1.86D Water = 1·84D.

Draw diagrammatic representations of the shapes of these molecules and indicate the directions of the moments in each case From what you know about the bond angles and the polarity of the bonds, suggest a possible explanation for the observed values. (*Delhi B Sc Hons I Year 1972*)

6 (*a*) Explain the terms 'conjugate acid and conjugate base' with suitable examples

(*b*) Arrange the following acids according to increasing acid strength, giving reasons for your answer Isobutyric acid, propionic acid, α-chloropropionic acid, β-chloropropionic acid. (*Delhi B Sc Hons I Year 1978*)

7 (*a*) How will you define an acid in terms of (*i*) Bronsted-Lowry, and (*ii*) Lewis concepts ? Give suitable examples.

(*b*) Giving reasons state which is the stronger acid in each of the following pairs

(*i*) H_3O^+ and H_2O ; (*ii*) NH_4^+ and NH_3 ;
(*iii*) H_2S and HS^- ; (*iv*) H_2O and OH^-

(*Delhi B Sc Hons I Year 1979, 73*)

8 (*a*) The bond angle in CH_4 is 109.5° How can this value be explained in terms of modern concepts ?

(*b*) Why is ethylene a planar molecule and acetylene a linear molecule ?

(*c*) How do bond length and bond strength vary in the following cases :

C–C, C=C, C—Cl ?

(*Delhi B Sc Hons I Year 1980*)

ANSWERS

3 (*a*) 5 (*b*) 1, 2, 3, 4 (*c*) 5 (*d*) 1. (*e*) 6.

(*f*) Carbon dioxide molecules are held together by van der Waals forces This accounts for its low sublimation temperature. High melting and boiling points of silica indicate the presence of strong bonds. This occurs because silicon forms four single bonds to four oxygen atoms, giving a network of solid.

Short Answer Type :

1. What are atomic numbers of elements whose outermost electrons are represented by : (*i*) $2p^3$; (*ii*) $3d^5$. (*Delhi B.Sc. 1976*)

2. How many electrons are there in the valency quantum level of copper (At. No =29) ? Give reasons. *(Delhi B Sc 1976)*

3. Which of the orbitals 1*p*, 2*s*, 2*p*, 3*f* are not possible ? Give reason *(Delhi B Sc 1976)*

4. Which of the electron distribution in the Be atom is correct in unexcited state (*i*) $1s^2, 2s^2$, (*ii*) $1s^2, 2s^1, 2p^1$? Give reason *(Delhi B Sc 1976)*

5 H_2O is a liquid while H_2S is a gas Explain why *(Delhi B Sc 1976)*

6 The melting point of NaCl is much higher than that of $AlCl_3$ Explain why ? *(Delhi B Sc 1976)*

7 In a molecule of N_2, there is one sigma bond and two pi bonds joining the two nitrogen atoms Explain *(Delhi B Sc 1976)*

8 Write down the canonical forms of the following structures

(*i*) $H_2N-CH=CH-CH=CH_2$

(*ii*) $H_2C=CH-CH=O$ *(Delhi B Sc Hons 1976)*

9 Write down

(*i*) The conjugate base of nitromethane

(*ii*) The conjugate acid of isopropyl alcohol *(Delhi B Sc Hons 1976)*

10 Explain the difference between electromeric and inductive effects, taking one suitable example in each case *(Delhi B Sc Hons 1976)*

11 Write down the different canonical forms of (*i*) acetamide (*ii*) methyl vinyl ketone *(Delhi B Sc Hons 1976)*

12 What is dipole moment ? What useful information can we get by measuring the dipole moment of a compound ? *(Delhi B Sc Hons 1976)*

13 The dipole moment of CO_2 is zero and that of diethyl ether is 1.12D Predict the shape of these molecules and indicate the direction of the moments in each case *(Delhi B Sc Hons 1980, 76)*

14 A neutral atom of an element has two K electrons eight L electrons and five M electrons Predict from this (*i*) atomic number (*ii*) the total number of *s* electrons, (*iii*) the total number of *p* electrons, (*iv*) the total number of *d* electrons *(Mysore B Sc 1974)*

15 Carbon-carbon double bond is shorter than carbon-carbon single bond Explain why *(Delhi B Sc Hons 1980 Kerala B Sc 1975)*

[Hint Since an *s* orbital is smaller than a *p* orbital the bond length of a molecular orbital decreases as the amount of *s* character in a hybrid orbital increases from sp^3 (25% *s* character) to sp^2 (33.3% *s* character) to *sp* (50% *s* character). Hence C=C involving sp^2 hybrid orbitals is shorter than C–C involving sp^3 hybrid orbitals.]

16 Carbon-carbon bond distance in benzene is intermediate between the bond distances in ethylene and ethane Account for this *(Delhi B Sc Hons 1980, Madras B Sc 1974)*

17 Write down the electronic structure of formaldehyde and indicate the σ-electrons, "π-electrons" and *n*-electrons (i.e. non bonded electrons)" in it *(Osmania B Sc 1975)*

18. Classify, giving suitable explanation, the following compounds as Lewis acids, Lewis bases, neither or both

(*i*) $AlCl_3$, (*ii*) BF_3, (*iii*) NH_3, (*iv*) C_6H_6,
(*v*) H_2O, (*vi*) C_2H_5ONa *(Delhi B Sc. 1977)*

19. What is the difference between resonance and tautomerism ? Explain your answer with examples. *(Delhi B.Sc. Hons 1977)*

[**Hint.** *See* chapter 11]

20. How will you define acid in terms of (*i*) Bronsted-Lowry, and (*ii*) Lewis concepts? Give suitable examples.

21. Discuss the variation of acid strength in the following compounds giving reasons. Arrange them in the descending order of their acid strength (*a*) HCOOH, (*b*) $ClCH_2COOH$, (*c*) CH_3COOH, (*d*) C_6H_5COOH.
(Delhi B.Sc.Hons. 1980 ; Andhra B.Sc. 1977)

22. Explain why

(*a*) Phenols are stronger acids than alcohols.

(*b*) Chloro-acetic is more acidic than acetic acid.

(*c*) Methylamine is more basic than ammonia.
(Andhra B.Sc. 1976)

23. Explain why alcohols have higher boiling points than the corresponding isomeric ethers *(Delhi B Sc. Hons. Sub 1978)*

8

Classification and Nomenclature of Organic Compounds

1. **Classification of Organic Compounds.**—The major groups into which organic compounds have been further classified are :

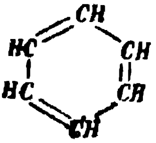
(1) **Open-chain or Acyclic Compounds.** Carbon compounds having open chains of carbon atoms, whether branched or unbranched, are referred to as **aliphatic compounds**. The name was derived from the Greek word *aleiphar* (meaning fat) and arose from the fact that first compounds of this class to be studied were the fatty acids. A few examples of this class are :

CH_4 ;	$CH_3—CH_2—CH_2—CH_3$;	$CH_3—CH_2—CH_2I$
Methane	Butane	*n*-Propyl iodide

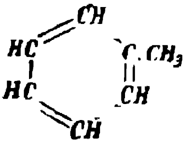
(2) **Closed-chain or Cyclic Compounds.** Organic compounds with a closed chain of atoms are termed as *closed-chain* or *cyclic compounds*. When a molecule contains two or more ring systems, it is said to be *polycyclic*. These are further sub-divided in accordance with the composition of the closed nucleus as follows :

(*a*) **Homocyclic or Carbocyclic Compounds.** The homocyclic or carbocyclic compounds are composed entirely of carbon atoms. These may be further sub-divided into two important groups, *viz.*,

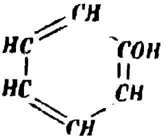
(*i*) **Aromatic Compounds.** Compounds having a ring of six carbon atoms of the benzene type are called *aromatic or benzenoid compounds*. Aromatic compounds occur chiefly in plants and many have fragrant smell, hence the name (Greek *aroma*=sweet smell). The following can be cited as examples of aromatic compounds :



Benzene

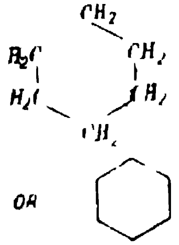


Toluene

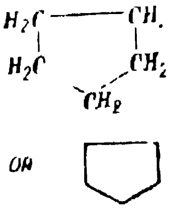


Phenol

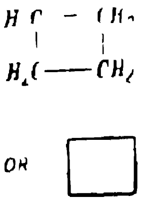
(*ii*) **Alicyclic Compounds.** Certain homocyclic compounds have a ring structure but are found to behave more like aliphatic compounds than aromatic. These have, therefore, been named as *aliphatic cyclic or alicyclic compounds* and include the important group of polymethylenes or their compounds, *e.g.*,



Cyclohexane or
Hexamethylene

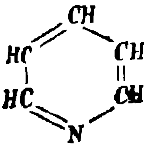


Cyclopentane or
Pentamethylene

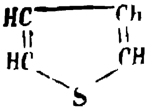


Cyclobutane or
Tetramethylene

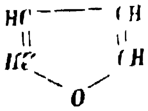
(*b*) **Heterocyclic Compounds** In heterocyclic compounds the rings include atoms of more than one kind. A few examples of this class are :



Pyridine



Thiophen

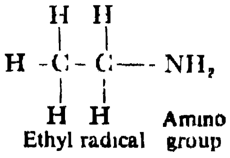


Furan

This scheme of classification may be summarized as follows :

Organic compounds
- Open-chain, acyclic, or aliphatic compounds, *e.g.*, methane, butane
- Closed chain or cyclic compounds
  - Homocyclic or carbocyclic compounds
    - Aromatic compounds, *e g*, benzene, toluene
    - Alicyclic compounds, *e g*, cyclobutane, cyclohexane
  - Heterocyclic compounds, *e g*, Pyridine, thiophen,

2. **Group or Radical.**—An organic compound is generally made up of two or more parts each of which is called a **group** or **radical**. Each group has its own typical characteristic properties. For example, ethylamine, $C_2H_5NH_2$ molecule is made up of : (*i*) ethyl radical, C_2H_5, (*ii*) amino group, NH_2.



$$\underbrace{\begin{matrix} & H & H & \\ & | & | & \\ H- & C- & C & \\ & | & | & \\ & H & H & \end{matrix}}_{\text{Ethyl radical}} \underbrace{-NH_2}_{\text{Amino group}}$$

The radicals determine to a great extent the properties of organic compounds. Identical chemical properties shown by all amines (methylamine, ethylamine, propylamine) are, in fact, the properties of amino group, called the *characteristic group* or the *functional group*.

3. **Homologous Series.**—As given above chemical properties of an organic compound are, in fact, the properties of the functional group present in it. The rest of the molecule simply affects the physical constants (*e.g.*, m.p., b.p., density, etc.) and has very little effect on the chemical properties. *A group or class of organic compounds each containing one particular characteristic group (or functional group) constitutes a* **homologous series.** Organic compounds have been classified into a number of homologous series.

Characteristics of a homologous series :

(*i*) Different members constituting a homologous series can be assigned a *general formula.*

(*ii*) Every member of the homologous series is known as the homologue of the other members and differs from its next higher or the next lower homologue by a *common difference*, CH_2. The homologues constitute, so to say, an arithmetical progression.

(*iii*) Various members can be prepared by *general methods of preparation* for the series.

(*iv*) Different members possess *similar chemical properties. In* fact *their chemical properties are the properties of the characteristic or the functional group* of the series.

(*v*) Their physical properties show a *gradation* with the rise of molecular weight.

For example, the homologous series of amines is as given below :

$C_nH_{2n+1}—NH_2$	*General Formula*
CH_3NH_2	*Methylamine*
$C_2H_5NH_2$	*Ethylamine*
$C_3H_7NH_2$	*Propylamine*
$C_4N_9NH_2$	*Butylamine*

4 **Nomenclature of Organic Compounds.**—When the first child is born in a family, the parents are quite fussy in naming the child. If, however, the number of children multiplies rapidly, naming a child becomes a routine. In early days when a new organic compound was discovered, the chemists usually named it on the basis of its history, *e.g.*, wood spirit was so called as it was obtained by the destructive distillation of wood. It was later on named methyl alcohol (Greek : *methu*=wine, and *hule*=*wood*). Similarly, acetic acid derives its name from vinegar (Latin : *acetum*=vinegar) of which it is the chief constituent. These names are called **common or Trivial names.**

As the number of organic compounds multiplied rapidly, naming each compound on the basis of history, etc., became a problem. The need for a systematic nomenclature was felt badly. The work of systematization was carried on by the *International Congress of Leading Chemists* held in Geneva in 1892. They formulated a comprehensive and rational system of nomenclature referred to as the **Geneva system** of nomenclature. Slight modifications and improvements have

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To the Student. Homologous compounds react alike because they have the same reactors (functional group). You should not attempt to memorize each equation but should concentrate on type reactions that are of general application to homologous series.

been made in this system from time to time, one of these being at Liege (Belgium) in 1930 by the *International Union of Chemists*. The modified scheme of nomenclature is also referred to as the **IUC system.** The IUC system has been somewhat further modified by the *International Union of Pure and Applied Chemists* in 1958 and is termed **IUPAC system.**

For naming a compound according to the IUPAC system we proceed as follows :

(*i*) Select the longest chain of carbon atoms.

(*ii*) Number the carbon chain from the end nearer to the substituents or functional group. Lowest number must be given to the carbon atom bearing the functional group.

(*iii*) Substituents/side chains are indicated by suitable prefixes whereas *the functional groups are indicated by suitable endings.*

(*iv*) *If* more than one prefixes are used, these must be arranged alphabetically.

These rules have been applied while naming various members of the different homologous series given below. A detailed account *of the IUPAC system of nomenclature has been given in the next* chapter.

The trend in our present-day nomenclature is towards the adoption and use of the IUPAC system but the common or trivial names which have been established by common usage cannot be ignored. The young chemists should, therefore, master both the systems of nomenclature.

The names of various homologous series and their particular members, which we come across in our study of aliphatic compounds, are given below :

(1) **Alkanes or Paraffins** (*Saturated hydrocarbons*). These are compounds of carbon and hydrogen with *general formula* C_nH_{2n+2}. These are characterised by linking of various carbon atoms to each other through single covalent linkages (C—C). Some particular members are :

CH_4 ;	C_2H_6 ;	C_3H_8 ;	C_4H_{10} ;	C_5H_{12} ;	C_6H_{14} ;
Methane	Ethane	Propane	Butane	Pentane	Hexane

In the case of first few alkanes, the trivial and the IUPAC names are identical.

HOMOLOGOUS SERIES NAMED AFTER ALKANES

(2) **Olefins or Alkenes** (*Unsaturated hydrocarbons*). These are characterized by the presence of a carbon-carbon double covalent linkage (C=C).

General Formula : C_nH_{2n}. *Characteristic group* : C=C

Members : The name derived from alkanes by substituting suffix *-ane* by *-ylene* (for common names) or *-ene* (in the IUPAC system). For example,

Alkane		*Alkene*	*Common name*	*IUPAC name*
CH_4	Methane	CH_2 (*unstable*)	Methylene	Methene
C_2H_6	Ethane	$C_2H_4(CH_2{=}CH_2)$	Ethylene	Ethene
C_3H_8	Propane	$C_3H_6(CH_3{-}CH{=}CH_2)$	Propylene	Propene
C_4H_{10}	Butane	C_4H_8	Butylene	Butene

(3) **Acetylene hydrocarbons or Alkynes** (*Unsaturated hydrocarbons*). The alkynes are characterised by presence of a carbon-carbon triple covalent linkage ($C{\equiv}C$).

General Formula : C_nH_{2n-2}. *Characteristic group* : $C{\equiv}C$

Members. These derive their names from alkanes by substituting the suffix *-ane* by *-yne.*

Alkane	*Alkyne*	*Common name*	*IUPAC name*
C_2H_6 Ethane	C_2H_2 ($CH{\equiv}CH$)	Acetylene	Ethyne
C_3H_8 Propane	C_3H_4 ($CH_3{-}C{\equiv}CH$)	Allylene	Propyne

(4) **Alkyl groups or radicals** (*Univalent frameworks derived from alkanes by the loss of one hydrogen atom*). Alkanes are represented by the general formula C_nH_{2n+2} or R—H where 'R' is always C_nH_{2n+1}. The group 'R' is termed as alkyl group and is a univalent radical.

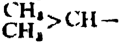
The *alkyl* groups derive their names from *Alkanes* by substituting the suffix *-ane* by *-yl.*

Alkanes		*Alkyl Groups*	
CH_4	Methane	CH_3-	Methyl
C_2H_6	Ethane	C_2H_5-	Ethyl
C_3H_8	Propane	C_3H_7-	Propyl
C_4H_{10}	Butane	C_4H_9-	Butyl

The propyl radical may be

$CH_3.CH_2.CH_2-$ Propyl radical

or

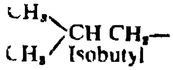


$$\begin{matrix}CH_3\\CH_3\end{matrix}{>}CH-$$

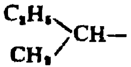
Isopropyl radical or 1-Methylethyl

The butyl radical may be

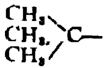
$CH_3.CH_2.CH_2.CH_2-$
Butyl



Isobutyl



sec-Butyl



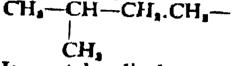
tert-Butyl

Note. A carbon atom attached to two other carbon atoms is termed *Secondary* and when attached to three other carbon atoms is called *Tertiary.* In *sec*-Butyl one valency of secondary carbon atom is free while in *tert*-Butyl one valency of a tertiary carbon atom is free.

Similarly the pentyl or amyl radical, $C_5H_{11}-$ may be

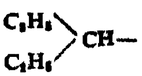
$(CH_3)_3C{-}CH_2-$, —Neopentyl
(having one quaternary C-atom)

$CH_3.CH_2.CH_2.CH_2.CH_2-$;
Pentyl

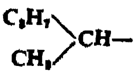


$$CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_2.CH_2-$$

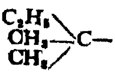
Isopentyl radical



1-Ethylpropyl



1-Methylbutyl



tert-Pentyl

Eight trivial names for branched alkyl groups recognized in 1957 IUPAC Rules are :

(*i*) *Isopropyl	or	1-Methylethyl
(*ii*) *Isobutyl	or	2-Methylpropyl
(*iii*) **sec*-Butyl	or	Methylpropyl
(*iv*) **tert*-Butyl	or	1, 1-Dimethylethyl
(*v*) *Isopentyl	or	3-Methylbutyl
(*vi*) *Neopentyl	or	2,2-Dimethylpropyl
(*vii*) **tert*-Pentyl	or	1,1-Dimethylpropyl
(*iii*) *Isohexyl	or	4-Methylpentyl

*For the unsubstituted group only.

(5) **Alkenyl groups**. (*Univalent residues derived from alkenes by loss of one hydrogen atom*). Some common alkenyl groups are :

Alkenyl radical	*Parent alkene*	*Common name*	*IUPAC name*
$CH_2=CH-$	$CH_2=CH_2$ ethene	Vinyl	Ethenyl
$CH_2=CH-CH_2-$	$CH_2=CH-CH_3$ propene	Allyl	2-Propenyl
$CH_3CH=CH-$	,,	—	1-Propenyl
C_4H_7-	C_4H_8(butene)	—	Butenyl

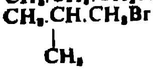
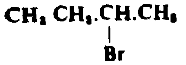
(6) **Alkynyl groups** (*Univalent residues derived from alkynes by loss of one hydrogen atom*). Some common alkynyl groups are :

Alkynyl group	*Parent alkyn*	*Common name*	*IUPAC name*
$CH\equiv C-$	$CH\equiv CH$ ethyne	—	Ethynyl
$CH\equiv C-CH_2-$	$CH\equiv C-CH_3$ propyne	Propargyl	2-Propynyl

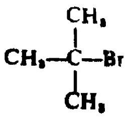
(7) **Alkyl halides**. These are monohalogen derivatives of the alkanes obtained by the replacement of one hydrogen atom by a halogen atom, X.

General formula : RX ; *Characteristic Group* : X.

Common names of alkyl halides are derived from the alkyl group present while in the IUPAC system these are named as substituted alkanes.

Formula	*Common name*	*IUPAC name*
$CH_3.Cl$	Methyl chloride	Chloromethane
$CH_3.CH_2Br$	Ethyl bromide	Bromoethane
$CH_3.CH_2CH_2I$	Propyl iodide	1-Iodopropane
$CH_3CHI.CH_3$	Isopropyl iodide	2-Iodopropane
$CH_3.CH_2.CH_2.CH_2Br$	Butyl bromide	1-bromobutane
 $\underset{\displaystyle CH_3}{CH_3.\underset{\vert}{C}H.CH_2Br}$	Isobutyl bromide	2-Methyl- 1-bromopropane
 $CH_3\,CH_2.\underset{\displaystyle Br}{\underset{\vert}{C}H}.CH_3$	*sec*-Butyl-bromide	2-Bromobutane

To the Students. The first step in learning Organic Chemistry is to learn Nomenclature of Organic Compounds. If you start reading preparation and properties of various organic compounds without mastering this, you are sure to complain that Organic Chemistry is difficult, uninteresting and above your head. Master this chapter and you will simply play with organic compounds.

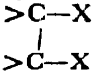
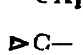
 $CH_3-C(CH_3)_2-Br$	*tert*-Butyl bromide	2-Bromo-2-methyl-propane

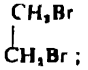
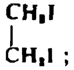
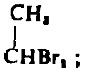
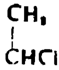
A few alkenyl halides and alkynyl halides are :

$CH_2=CH-Cl$	Vinyl chloride	Chloroethene
$CH_2=CH-CH_2Cl$	Allyl chloride	3-chloro-1-propene
$CH\equiv C-CH_2Cl$	Propargyl chloride	3-chloro-1-propyne

(8) **Dihalogen derivatives.** The dihalogen derivatives of alkanes are obtained by replacement of two hydrogen atoms by two atoms. If the two halogen atoms are attached to the same carbon atom, the derivative is called an alkylidene halide, whereas it is termed alkylene halide if the two halogen atoms are attached to two different carbon atoms. Hence for the dihalogen derivatives,

General Formula : $C_nH_{2n}X_2$

Characteristic Group :	*Alkylene halide*	*Alkylidene halide*
	 $>C-X$ $>C-X$ Two halogen atoms attached to different carbon atoms	 $-CX_2$ $>C-$ Two halogen atoms attached to the same carbon atom

Members :	 CH_2Br-CH_2Br ;	 CH_2I-CH_2I ;	 CH_3-CHBr_2 ;	 CH_3-CHCl_2
Common name :	Ethylene bromide	Ethylene iodide	Ethylidene bromide	Ethylidene chloride
IUPAC name :	1,2-dibromoethane	1,2-diiodoethane	1,1-dibromoethane	1,1-dichloroethane

(9) **Tri- and Tetra-halogen derivatives.** Like dihalogen derivatives we have for tri- and tetra-halogen derivatives :

General Formula : $C_nH_{2n-1}X_3$ and $C_nH_{2n-2}X_4$

Characteristic Group : X_3 *and* X_4

Members :			
	$CHCl_3$;	CHI_3	CCl_4
	Chloroform or Trichloromethane	Iodoform or Triiodomethane	Carbon tetrachloride or Tetrachloromethane

(10) **Monohydric saturated Alcohols or Alkanols.** Hydroxy derivatives of alkanes are called alcohols. Those obtained by the replacement of one hydrogen atom by one hydroxyl group are called *monohydric alcohols*. Thus for monohydric alcohols, we have

General Formula : $C_nH_{2n+1}OH$ or ROH

Characteristic Group $-OH$

Alcohols are named after the alkyl group present (*Common names*) or after the alkane from which these are derived (IUPAC system of nomenclature). The final *e* of the alkane is replaced by *-ol*. Some particular members of the series are :

***Formula* :**	CH_3OH ;	C_2H_5OH ;	C_3H_7OH ;	C_4H_9OH
***Common name* :**	Methyl alcohol or	Ethyl alcohol or	Propyl alcohol or	Butyl alcohol or
***IUPAC name* :**	Methanol	Ethanol	Propanol	Butanol

Two propanols are :

$CH_3.CH_2.CH_2OH$; $CH_3.CHOH.CH_3$

1-Propanol or Propyl alcohol* ; 2-Propanol or Isopropyl alcohol

Similarly, write four butyl alcohols.

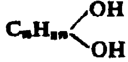
The common unsaturated alcohols we come across are :

$CH_2{=}CHOH$ — Vinyl alcohol (*Unstable*)

$CH_2{=}CH-CH_2OH$ — Allyl alcohol, 2-Propene-1-ol

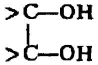
(11) **Dihydric alcohols, Glycols or Alkanediols.** The dihydroxy derivatives of alkanes are termed dihydric alcohols or glycols. For the homologous series :

General formula :



$C_nH_{2n}(OH)_2$

Characteristic Group :

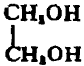


$$\begin{array}{l}>C-OH\\ \quad|\\ >C-OH\end{array}$$

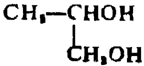
Two —OH groups attached to different C-atoms.

The common names of glycols are derived from the corresponding olefins. According to the IUPAC system of nomenclature, the class suffix is *-diol* and these are taken as derivatives of alkanes. For example,

Formula :



$$\begin{array}{l}CH_2OH\\ |\\ CH_2OH\end{array}$$



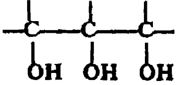
$$\begin{array}{l}CH_3-CHOH\\ \qquad\;|\\ \qquad\;CH_2OH\end{array}$$

Common name :	Ethylene glycol or	Propylene glycol or
IUPAC name :	1,2-Ethanediol	1 2-Propanediol

(12) **Trihydric Alcohols or Alkanetriols.** These are trihydroxy derivatives of alkanes with

General Formula : $C_nH_{2n-1}(OH)_3$

Characteristic Group :



$$\begin{array}{ccccc}|&&|&&|\\ -C&-&C&-&C-\\ |&&|&&|\\ OH&&OH&&OH\end{array}$$

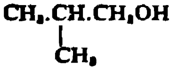
Three —OH groups attached to three different carbon atoms.

$CH_2(OH)—CH(OH)—CH_2OH$, Glycerol or 1, 2, 3-*Propanetriol* is the most important member of the homologous series.

Note. Use of prefixes like *n*, *iso*, *sec*, *tert* and *neo-* with different alkyl groups must be avoided while writing IUPAC names. For example

(*i*) $CH_3.CH_2.CH_2CH_3$ is to be named as butane and not as *n*-butane.

(*ii*)

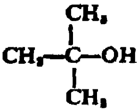


$$\begin{array}{l}CH_3.CH.CH_2OH\\ \qquad\;|\\ \qquad\;CH_3\end{array}$$

is to be named as 2-methyl-1-propanol and not as isobutanol.

(*iii*) $CH_3.CH_2.CHOH.CH_3$ is to be named as 2-Butanol and not as *sec*-Butanol.

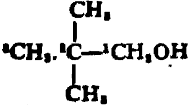
(*iv*)



$$\begin{array}{c}CH_3\\ |\\ CH_3-C-OH\\ |\\ CH_3\end{array}$$

is to be named as 2-methyl-2-propanol and not as *tert*-Butanol.

(*v*)



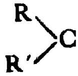
$$\begin{array}{c}CH_3\\ |\\ {}^1CH_3.{}^2C-{}^3CH_2OH\\ |\\ CH_3\end{array}$$

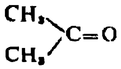
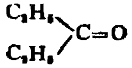
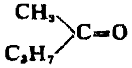
Neopentyl alcohol (*Common name*)

is to be named 2, 2-dimethyl-1-propanol and not *neo*-pentanol.

(13) **Ethers or Alkoxyalkanes.** The general formula of the ethers is R—O—R' with —O— as the characteristic group. When the two alkyl groups are the same, the ether is said to be simple while another with two different alkyl groups is termed mixed ether. Some particular members are :

Formula	*Common name*	*IUPAC name*
$CH_3.O.CH_3$	Methyl ether or dimethyl ether (*simple*)	Methoxymethane
$C_2H_5.O.CH_3$	Ethyl methyl ether (*mixed*)	Methoxyethane
$C_2H_5.O\ C_2H_5$	Ethyl ether or Diethyl ether (*simple*)	Ethoxyethane

(14) **Ketones or Alkanones.** The functional group of ketones is $>C=O$ and their general formula is  $\begin{matrix}R\\R'\end{matrix}\!\!>C=O$. Like ethers, ketones may be simple or mixed. The lower members are commonly named according to the alkyl groups attached to the ketonic groups. In the IUPAC system, ketones are designated by the suffix *-one* which is added to the name of the hydrocarbon from which they are derived. A few particular members are :

Formula of the Ketone	*Common name*	*IUPAC name*
 $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=O$	Dimethyl ketone or Acetone	Propanone (*Simple*)
$CH_3\,CH_2\,CO.CH_2.CH_3$ or  $\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!\!>C=O$	Diethyl ketone (*Simple*)	3-Pentanone
$CH_3.CO.CH_2.CH_2.CH_3$ or  $\begin{matrix}CH_3\\C_3H_7\end{matrix}\!\!>C=O$	Methyl propyl ketone	2-Pentanone (*Mixed*)

(15) **Thioalcohols, Thiols or Mercaptans.** The general formula of thioalcohols is R—SH with —SH as the characteristic group. Thioalcohols are named after the alkyl group present (*common names*) or after the alkane from which these are derived (*IUPAC names*). The suffix *thiol* is added to the name of the alkane. Some particular members are :

Formula :	CH_3SH	C_2H_5SH	C_3H_7SH	C_4H_9SH :
Common name :	Methyl thioalcohol or Methyl mercaptan	Ethyl thioalcohol or Ethyl mercaptan	Propyl thioalcohol or Propyl mercaptan	Butyl thioalcohol or Butyl mercaptan
IUPAC name :	Methanethiol	Ethanethiol	Propanethiol	Butanethiol

(16) **Thioethers or Alkyl sulphides.** The general formula for thioethers is R—S—R with —S— as the characteristic group. These are ethers in which the oxygen atom has been replaced by sulphur. They are named by adding the prefix *thio-* to the name of the corresponding ether. Some individual members are :

Formula	*Name*
$CH_3—S—CH_3$	Dimethyl sulphide or Methyl thioether
$C_2H_5—S—C_2H_5$	Diethyl sulphide or Ethyl thioether.

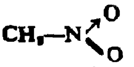
In the IUPAC system RS group is termed alkylthio and thioethers are named as (alkylthio) alkanes. For example

Formula	*IUPAC Name*
CH_3-S-CH_3	(Methylthio) methane
$C_2H_5-S-C_2H_5$	(Ethylthio) ethane

(17) **Alkyl Nitrite.** This group of compounds is assigned the general formula $R-O-N=O$ with $-O-N=O$ as the functional group. Nitrogen is trivalent in the nitrite radical. Some particular members are :

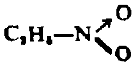
$CH_3-O-N=O$	Methyl nitrite
$C_2H_5-O-N=O$	Ethyl nitrite
$C_3H_7-O-N-O$	Propyl nitrite
$C_4H_9-O-N=O$	Butyl nitrite

(18) **Nitroparaffins or Nitroalkanes.** These are named as the nitro derivatives of the corresponding paraffins. The general formula of the homologous series is $R-N\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix}$ with $-N\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix}$ as the functional group. Nitrogen is pentavalent in a nitro group (*cf.* nitrite). Some individual members are :



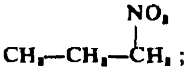
$CH_3-N\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix}$:

Nitromethane



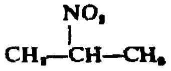
$C_2H_5-N\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix}$:

Nitroethane



$CH_3-CH_2-\underset{}{\overset{NO_2}{\overset{|}{C}}}H_2$;

1-Nitropropane



$CH_3-\overset{NO_2}{\overset{|}{C}}H-CH_3$

2-Nitropropane

(19) **Amines.** Alkyl derivatives of ammonia (NH_3) are called amines. These are called primary, secondary or tertiary depending upon the number of hydrogen atoms of NH_3 replaced. Individual members are named according to the alkyl group or groups attached to the nitrogen atom while *amine* remains as the suffix in each case.

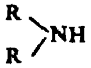
Primary Amines

General formula : $R-NH_2$: *Characteristic Group* : $-NH_2$

Members : CH_3NH_2 ; Methylamine $C_2H_5NH_2$; Ethylamine $C_3H_7NH_2$; Propylamine $C_4H_9NH_2$; Butylamine

Secondary Amines

General Formula :

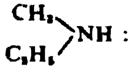


$\begin{smallmatrix}R\searrow\\ R\nearrow\end{smallmatrix}NH$:

Characteristic Group :

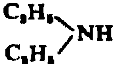
$\begin{smallmatrix}\searrow\\ \nearrow\end{smallmatrix}NH$

Members $(CH_3)_2NH$; Dimethylamine (*Simple*)



$\begin{smallmatrix}CH_3\searrow\\ C_2H_5\nearrow\end{smallmatrix}NH$:

Ethylmethylamine (*Mixed*)



$\begin{smallmatrix}C_2H_5\searrow\\ C_2H_5\nearrow\end{smallmatrix}NH$

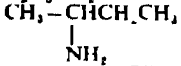
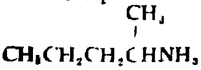
Diethylamine (*Simple*)

Tertiary Amines

General Formula : R_3N : *Characteristic Group* : $\equiv N$

Members : $(CH_3)_3N$: Trimethylamine $(C_2H_5)_3N$ Triethylamine

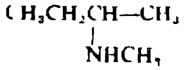
In the IUPAC system primary monoamines are preferably named substitutively by adding the suffix *amine* to the name of the chain or ring system to which the NH_2 group is attached. Terminal *e* of the alkane is omitted. For example,

Formula	*IUPAC Name*
CH_3NH_2	Methanamine or Methylamine
$C_2H_5NH_2$	Ethanamine or Ethylamine
 $CH_3-\underset{\mid}{\underset{NH_2}{CH}}CH_2CH_3$	2 Butanamine or *sec*-Butylamine
 $CH_3CH_2CH_2\overset{CH_3}{\overset{\mid}{C}}HNH_2$	2-Pentanamine

Secondary and tertiary amines are preferably named as derivatives of the highest ranking primary amine structure present. For example,

$CH_3CH_2CH_2NHCH_3$ is termed *N*-Methyl-1-propanamine.

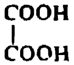
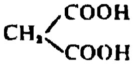
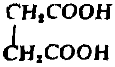
As alternatives to alkanamine-type names for the secondary and tertiary amines, substitutive names as alkyl derivatives of NH_3 are acceptable, as given below :

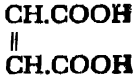
Formula	*IUPAC Name*
 $CH_3CH_2\underset{\mid}{\underset{NHCH_3}{CH}}-CH_3$	*N*-Methyl-2-butanamine
$CH_3CH_2NHCH_2CH_3$	*N*-Ethylethanamine or Diethylamine
$(CH_3CH_2)_3N$	*N*, *N*-diethylethanamine or Triethylamine

(20) **Fatty acids, Mono-carboxylic acids or Alkanoic acids**. A carboxyl group (—COOH) is the *functional group* of fatty acids while RCOOH is their *general formula*. Their IUPAC names are derived from the name of the corresponding alkanes by replacing the final *-e* with *-oic* and adding the word acid as shown below :

Formula	*Common name*	*IUPAC name*
HCOOH	Formic acid	Methanoic acid
CH_3COOH	Acetic acid	Ethanoic acid
C_2H_5COOH	Propionic acid	Propanoic acid
C_3H_7COOH	Butyric acid	Butanoic acid
C_4H_9COOH	Valeric acid	Pentanoic acid

(21) **Dibasic acids. Dicarboxylic acids or Alkanedioic acids**. These can be represented by the general formula $C_nH_{2n}(COOH)_2$ wherein two carboxyl groups constitute the *functional group*. Some typical members are :

Formula	*Common name*	*IUPAC name*
 $\begin{matrix}COOH\\ \mid\\ COOH\end{matrix}$	Oxalic acid	Ethanedioic acid or Dicarboxylic acid
 $CH_2\begin{matrix}\diagup COOH\\ \diagdown COOH\end{matrix}$	Malonic acid	Propanedioic acid or Methanedicarboxylic acid.
 $\begin{matrix}CH_2COOH\\ \mid\\ CH_2COOH\end{matrix}$	Succinic acid	Butanedioic acid or 1, 2-Ethanedicarboxylic acid.

In addition to the above saturated dibasic acids,  $\begin{matrix}CH.COOH\\ \parallel\\ CH.COOH\end{matrix}$

is the formula representing butenedioic acids (maleic and fumaric acids)—two important unsaturated dibasic acids.

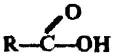
HOMOLOGOUS SERIES NAMED AFTER ACIDS

(22) **Aldehydes or Alkanals.** The aldehydes are represented by the *general formula* RCH=O or RCHO wherein —CH=O or —CHO constitutes the functional group.

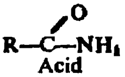
Their trivial names are derived from the acids which they give on oxidation by replacing the suffix *-ic acid* by *aldehyde*. In the IUPAC nomenclature the name of an aldehyde is derived from the corresponding alkane by replacing the final *e* by *al* as given below :

Formula	*Corresponding acid*	*Common name*	*IUPAC name*
$HCHO \xrightarrow{O}$	$HCOOH$ Formic acid	Formaldehyde	Methanal
$CH_3CHO \xrightarrow{O}$	CH_3COOH Acetic acid	Acetaldehyde	Ethanal
$C_2H_5CHO \xrightarrow{O}$	C_2H_5COOH Propionic acid	Propionaldehyde	Propanal
$C_3H_7CHO \xrightarrow{O}$	C_3H_7COOH Butyric acid	Butyraldehyde	Butanal

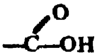
(23) **Acid amides.** These are compounds in which the hydroxyl group present in the carboxyl group of an acid has been replaced by the amino group (—NH_2).


$R-\overset{O}{\overset{/}{C}}-OH$

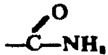
Carboxylic acid


$R-\overset{O}{\overset{/}{C}}-NH_2$

Acid amide


$-\overset{O}{\overset{/}{C}}-OH$

Carboxyl group

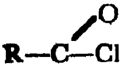
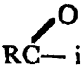

$-\overset{O}{\overset{/}{C}}-NH_2$

Amido group

Their common names have been obtained by replacing the suffix *-ic acid* of the corresponding acid by *amide*. According to the IUPAC system, the final *e* of the parent alkane is replaced by *amide*.

Formula	*Parent acid*	*Common name*	*Parent alkane*	*IUPAC name*
$HCONH_2$	$HCOOH$ Formic acid	Formamide	Methane	Methanamide or Formamide
CH_3CONH_2	CH_3COOH Acetic acid	Acetamide	Ethane	Ethanamide or Acetamide
$C_2H_5CONH_2$	C_2H_5COOH Propionic acid	Propionamide	Propane	Propanamide
$C_3H_7CONH_2$	C_3H_7COOH Butyric acid	Butyramide	Butane	Butanamide

(24) **Acid chlorides or Acyl chlorides.** The acyl chlorides may be prepared by replacement of the hydroxyl group in the carboxyl group by chlorine. Their general formula is

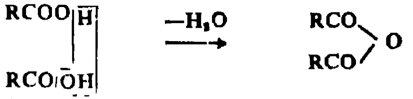

$R-\overset{O}{\overset{/}{C}}-Cl$ wherein  $R\overset{O}{\overset{/}{C}}-$ is called the acyl radical.

To the Student. Note carefully the suffix for an alcohol and an aldehyde ol is methyl alcohol whereas methanal is formaldehyde.

Their names are derived from the corresponding acids by replacing the suffix *-ic acid* by *-yl chloride* as illustrated below :

Formula	*Parent acid*	*Common name*	*IUPAC name*
$HCOCl$	$HCOOH$ Formic or Methanoic acid	Formyl chloride	Methanoyl chloride or Formamide
CH_3COCl	CH_3COOH Acetic or Ethanoic acid	Acetyl chloride	Ethanoyl chloride Acetamide
C_2H_5COCl	C_2H_5COOH Propionic or Propanoic acid	Propionyl chloride	Propanoyl chloride
C_3H_7COCl	C_3H_7COOH Butyric or Butanoic acid	Butyryl chloride	Butanoyl chloride

(25) **Acid anhydrides.** The acid anhydrides may be regarded *theoretically* as being derived from an acid by the removal of the molecule of water from two molecules of the acid.



Two molecules of an acid

Acid anhydride (General Formula)

These are named as the anhydrides of the acid radicals present, *e.g.*,

Formula	*Parent acid*	*Common name*	*IUPAC name*
$\left.\begin{array}{l}CH_3CO\\CH_3CO\end{array}\right>O$	CH_3COOH Acetic acid or Ethanoic acid	Acetic anhydride	Ethanoic anhydride or Acetic anhydride
$\left.\begin{array}{l}C_2H_5CO\\C_2H_5CO\end{array}\right>O$	C_2H_5COOH Propionic or Propanoic acid	Propionic anhydride	Propanoic anhydride or Propionic anhydride

(26) **Esters.** The esters are formed when the hydrogen atom in the carboxyl group is replaced by an alkyl group.

RCOOH	RCOOR′	—COOR′
Carboxylic acid	Ester **(General Formula)**	**Functional Group of an ester**

These are named as the alkyl salts of the parent acid as given below :

Formula of the Ester	*Parent acid*	*Common name*	*IUPAC name*
$HCOO.CH_3$	$HCOOH$ Formic or Ethanoic acid	Methyl formate	Methyl methanoate
$CH_3COO.CH_3$	CH_3COOH Acetic or Ethanoic acid	Methyl acetate	Methyl ethanoate
$C_2H_5COOC_2H_5$	C_2H_5COOH Propionic or Propanoic acid	Ethyl propionate	Ethyl propanoate
$C_3H_7COOC_2H_5$	C_3H_7COOH Butyric or Butanoic acid	Ethyl butyrate	Ethyl butanoate

(27) **Alkyl cyanides, Nitriles or Carbonitriles.** The *functional group* of alkyl cyanides is the —CN or —C≡N group whereas R—CN or R—C≡N is their *general formula.*

These are commonly named either as the alkyl cyanides or as the nitrile of the acid which is produced on their hydrolysis by changing the suffix *-ic acid* by *-onitrile.*

Their IUPAC names, however, follow the parent alkane as illustrated below :

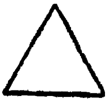
Formula		*Acid formed on hydrolysis*	*Common name*	*IUPAC name*
HCN	$\xrightarrow{H_2O}$	HCOOH Formic acid	Hydrogen cyanide or Formonitrile	Methanenitrile
CH_3CN	$\xrightarrow{H_2O}$	CH_3COOH Acetic acid	Methyl cyanide or Acetonitrile	Ethanenitrile
C_2H_5CN	$\xrightarrow{H_2O}$	C_2H_5COOH Propionic acid	Ethyl cyanide or Propiononitrile	Propanenitrile

(28) **Alkyl isocyanides, or Isonitriles.** These may be regarded as derivatives of alkanes formed by replacement of one hydrogen atom by the —NC or —$N\overset{\rightarrow}{=}C$ group which constitutes their *functional group.* They may be represented by the *general formula* R—NC or R—$N\overset{\rightarrow}{=}C$. Their common names follow from the alkyl group present. Their isonitrile names follow from the isomeric nitriles. For example, CH_3CN is acetonitrile and CH_3NC is acetoisonitrile.

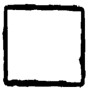
According to IUPAC recommendations, members of the class RNC, properly called isocyanides, should be named substitutively. As a substituent NC is termed carbylamino. Thus CH_3NC is carbylaminomethane and so on. Radicofunctional names such as phenyl isocyanide are not recommended. The class name isonitriles is also not recommended. Older names based on "carbylamine" have lergely disappeared and should not be revived.

Formula	*Common name*	*IUPAC name*
CH_3NC	Methyl isocyanide or Acetoisonitrile	Carbylaminomethane
C_2H_5NC	Ethyl isocyanide or Propionoisonitrile	Carbylaminoethane
C_3H_7NC	Propyl isocyanide or Butyroisonitrile	Carbylaminopropane

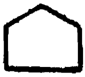
(29) **Alicyclic compounds.** The word alicyclic is derived from *aliphatic* and *cyclic* since these compounds are cyclic but resemble aliphatic compounds. Thus corresponding to alkanes, alkenes and alkynes we have cycloalkanes, cycloalkenes and cycloalkynes. Some examples of alicyclic compounds are :



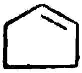
Cyclopropane
or Trimethylene

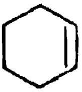


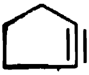
Cyclobutane
or Tetramethylene

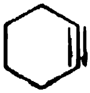


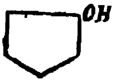
Cyclopentane
or Pentamethylene


Cyclopentene

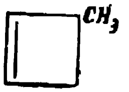

Cyclohexene


Cyclopentyne

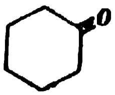

Cyclohexyne



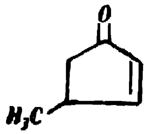
Cyclopentanol



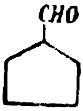
3-Methyl-cyclobutene



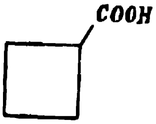
Cyclohexanone



4-Methyl-2-cyclobuten-1-one



Cyclopentane-carbaldehyde



Cyclobutane-carboxylic acid

5. Position of Numerals used in the Enumeration of Substituents.—Numerals representing location of unsaturation or functional groups are placed before the name stem. For example

2-Pentene	*not* Pent-2-ene ; *not* Pentene-2
1-Chloro-2-pentene	*not* 1-Chloropent-2-ene *not* 1-Chloropentene-2
1-Hexen-3-yne	*not* Hex-1-en-3-yne *not* 1-Hexenyne-3
1,5-Pentanediol	*not* Pentane-1,5-diol *not* Pentanediol-1,5

When locants for unsaturation and the principal function are required in the same name the locant(s) for unsaturation immediately proceeds the name of the parent compounds and the locant(s) for the functional group immediately precedes the suffix, for example, 2 Hexen-1-ol *not* 2-Hexenol-1.

6. Writing of Names.—The names of radicals replacing hydrogen atoms in a compound are "run on" while writing the name of a compound. For example, chlorotoluene, 2-nitrobutane, ethylpropylcarbinol, etc. If, however, the compound is named by any general term, the name of each part is written separately. For example, methyl alcohol, ethyl methyl ketone, methyl propyl ether, formic acid, acetaldehyde oxime (but acetaldoxime).

7. Elision of Vowels.—To avoid ambiguity vowels, whether pronounced or silent, are generally retained in the systematic names. This results very often in double vowels. For example, cyclooctane and chloroacetic acid.

However, it has become an accepted practice to elide the vowels *a*, *e* and *o* in the following circumstances :

(*i*) When preceding the suffix name of a functional group, *e.g.*,

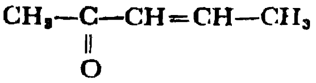
Propanol *not* Propaneol

Hexanamine *not* Hexaneamine

(*ii*) When a double bond and a triple bond are present together in the same chain or ring system and are, therefore, named sequentially as suffix, *e.g.*,

Pentenyne *not* Penteneyne

Elision of vowels is not affected by inserting locants, etc. into the name, *e.g.*,



$$CH_3—\underset{\underset{O}{\|}}{C}—CH=CH—CH_3$$

is 4-Hexen-2-one *not* 4-Hexene-2-one

8. **Punctuation Marks.**—Most commonly used punctuation marks in systematic names are hyphens and commas.

Hyphens are used to connect numbers and letters serving as locants or descriptive symbols to the syllabic portion of the name. For example,

2-Chloropropane 1-Bromo-4-chlorobutane,
N-methylaniline ($C_6H_5NHCH_3$)

Configurational prefixes like *cis* and *trans* or structure-defining prefixes like *sec* and *tert* are set off with hyphens, and written in italics, *e.g.*,

cis-2-Butene *trans*-Butene

sec-Butyl alcohol *tert*-Butyl alcohol

Structure-defining prefixes like cyclo, iso and neo are, however, considered to be an integral part of the name in which they are used. These are, therefore, neither separated by hyphens, nor written in italics, *e.g.*,

Cyclobutane *not cyclo*-Butane

Isobutane *not iso*-Butane

Neopentane *not neo*-Pentane

Commas are used to separate the individual members of a series of locants, *e.g.*, 1,1,2-Trichloroethane and 1,4-Butadiene.

Enclosing Marks. Parentheses ( ) and square brackets [ ] are used as demarcation symbols when the locants relate to names of complex groups, *e.g.*, $H_2NCH_2CH_2CH_2CONHCH_2CH_2OH$ is 4-Amino-*N*-(2-hydroxyethyl)butyramide.

Note. English letters used as locants, whether capital or lower-case are printed in italics, *e.g.*, *p*-xylene; *o*-Dichlorobenzene, *s*-trinitrotoluene, etc.,

QUESTIONS

1. What is the functional group and general formula for each of the following homologous series ?

Alkanes
Alkenes
Alkynes
Alcohols
Ethers
Aldehydes
Ketones
Amines
Esters
Acids
Acid amides
Acid chlorides
Alkyl cyanides
Nitroparaffins
Isocyanides

2. Write formulae for the following organic compounds :

Methane
Ethylene
Acetylene
Propane
Chloroform
Methanethiol
Acetone
Glycol
Glycerol
Iodoform
Methanal
Ethyl iodide
Ethylidene chloride
Ethylene bromide
Ethyl alcohol
Acetic acid
Propionic anhydride
Acetyl chloride
Ethyl acetate
Methyl propionate
Ethanoic acid
Ethyl mercaptan
Ethylamine
Acetaldehyde
Ethyl thioether
Formamide
Oxalic acid
Triethylamine
Succinic acid
Maleic acid
Acetonitrile
2-Propanol
Dimethylamine

3 What do you understand by IUPAC nomenclature ? Give names of the following compounds according to the IUPAC nomenclature and write their formulae :

Acetylene
Propylene
Acetone
Glycerol
Acetonitrile
Ethyl alcohol
Ethylene glycol
Formic acid
Acetyl chloride
Methyl propionate
Oxalic acid
Acetaldehyde
Propionamide
Acetic anhydride
Ethyl isocyanide

4. Give common names of the following compounds named according to the IUPAC system of nomenclature and write their formulae :

Ethane
Butene
Propanone
Ethanal
Methanol
Butanal
1,2-Ethane diol
1,2,3-Propanetriol
3-Pentanone
Pentanamide
Methyl ethanoate
carbylaminoethane
Ethanoic acid
Propanedioic acid
Ethanoyl chloride
Propanoic anhydride
Ethanenitrile
2-Chloropropane

5. Write formulae of the following compounds :

Cyclohexane
Cyclobutene
Cyclopentyne
3-Methylcyclohexene
3-Ethyl-1, 1-dimethylcyclohexanone
4-Bromo-4-methylcyclohexanone
3-Methlcyclopentene
4-Methyl-2-cyclopenten-1-one

6. Write various possible structures for the following molecular formulae and give their trivial as well as IUPAC names :

(*a*) C_4H_9Br ; (*b*) $C_4H_{10}O$; (*c*) $C_5H_{11}Cl$; (*d*) $C_5H_{12}O$;
(*e*) C_3H_6O ; (*f*) $C_4H_8O_2$; (*g*) C_2H_7N ; (*h*) C_3H_9N ;
(*i*) $C_5H_{10}O$; (*j*) C_5H_{10} ; (*k*) C_4H_6.

7. Write the possible structures for a compound having the molecular formula C_4H_8. Give their IUPAC names. *(Delhi B.Sc. Hons. 1971)*

8 Write the IUPAC names for the various compounds represented by the molecular formula $C_5H_{10}O$. *(Delhi B.Sc. Hons. 1973)*

9. Give the structural formulae of—

(*i*) Methoxyethane
(*ii*) 2-Butyne
(*iii*) 2-Methyl-1-butanol
(*iv*) 2-Methyl-3-pentanone

(Delhi B.Sc. 1976)

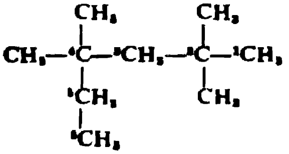
9

IUPAC System of Nomenclature

1. Naming Complex Compounds.—In spite of the fact that the trend in our present-day nomenclature is towards the adoption of the IUPAC system, the common names are still being used. In the case of complex compounds it has been found rather difficult to search for trivial names. On the other hand, IUPAC names are found handy and convenient. Various rules to be borne in mind while naming such compounds according to the IUPAC system are given in the following sections.

2. Longest Chain Rule.—In the given compound the *longest possible chain of carbon atoms is picked up and the compound is named as derivative of this alkane.*

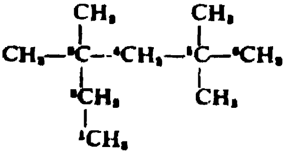
For example, in the compound X given below there are only five carbon atoms in the horizontal line, but we can select a six-carbon atom chain as indicated. The compound should, therefore, be considered as substituted hexane.



$$CH_3-\overset{CH_3}{\underset{\underset{{}^6CH_3}{{}^5CH_2}}{{}^4C}}-{}^3CH_2-\overset{CH_3}{\underset{CH_3}{{}^2C}}-{}^1CH_3$$

(2,2,4,4-tetramethylhexane)

Right



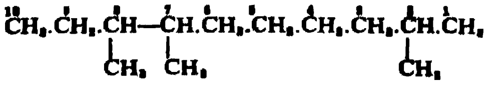
$$CH_3-\overset{CH_3}{\underset{\underset{{}^1CH_3}{{}^2CH_2}}{{}^3C}}-{}^4CH_2-\overset{CH_3}{\underset{CH_3}{{}^5C}}-{}^6CH_3$$

(3,3,5,5-tetramethylhexane)

Wrong

3. Lowest Number Rule.—The carbon chain is numbered from one end to the other by Arabic numerals and the positions of the side-chains are indicated by the numbers of C-atoms to which these are attached. The numbering is started from the end nearest to the substituents so as to give the lowest numbers possible to the side-chains.

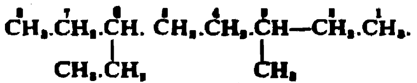
For example, the compound X is 2, 2, 4, 4-tetramethylhexane and not 3, 3, 5, 5-tetramethylhexane since the former uses lower numbers. Similarly,



$${}^{10}CH_3.{}^9CH_2.\underset{CH_3}{{}^8CH}-\underset{CH_3}{{}^7CH}.{}^6CH_2.{}^5CH_2.{}^4CH_2.{}^3CH_2.\underset{CH_3}{{}^2CH}.{}^1CH_3$$

is named 2, 7, 8-trimethyldecane and *not* 3, 4, 9 trimethyldecane since 2 in the first set is lower than 3 in the second set.

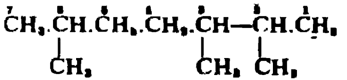
If different alkyl groups are in equivalent positions in relation to the ends of the chain, preference is given to the end where the radical has fewer carbon atoms (methyl, ethyl, etc.). For example,



$$\overset{8}{C}H_3.\overset{7}{C}H_2.\underset{CH_3.CH_2}{\overset{6}{C}H}.\ \overset{5}{C}H_2.\overset{4}{C}H_2.\underset{CH_3}{\overset{3}{C}H}—\overset{2}{C}H_2.\overset{1}{C}H_3.$$

is 6-ethyl-3-methyloctane (the methyl radical determines the end where the numbering begins).

If identical radicals are at equal distances from the ends, the chain is numbered from the end where there are more branches. For example,



$$\overset{7}{C}H_3.\underset{CH_3}{\overset{6}{C}H}.\overset{5}{C}H_2.\overset{4}{C}H_2.\underset{CH_3}{\overset{3}{C}H}—\underset{CH_3}{\overset{2}{C}H}.\overset{1}{C}H_3$$

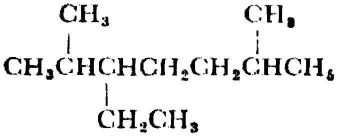
is 2, 3, 6-trimethylheptane and *not* 2, 5, 6-trimethylheptane.

If two sets of numbers be equally possible, the order of prefixes in the name will decide which set should be used. For example the compound given below

$^1CH_2Br—^2CH_2—^3CH_2—^4CH_2Cl$	$^4CH_2Br—^3CH_2—^2CH_2—^1CH_2Cl$
1-bromo-4-chlorobutane	4-bromo-1-chlorobutane
Right	**Wrong**

is 1-bromo-4-chlorobutane and not 4-bromo-1-chlorobutane although the numbers used in either case are the same (1, 4).

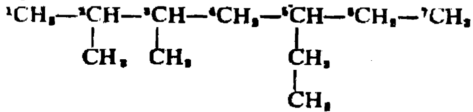
If chains of equal length are competing for selection as the parent chain in a branched alkane, the choice goes to the chain carrying greater number of side chains. For example



$$CH_3\overset{CH_3}{C}H\underset{CH_2CH_3}{C}HCH_2CH_2\overset{CH_3}{C}HCH_3$$

is 3-Ethyl-2, 6-dimethylheptane *not* 5-Isopropyl-2-methylheptane.

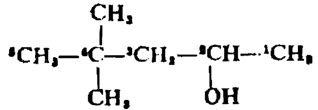
4. **Arrangement of Prefixes.**—In case more than one groups are attached to the chain, these should be arranged alphabetically. While doing so prefixes *di* and *tri* are not considered. For example,



$$^1CH_3—\underset{CH_3}{^2CH}—\underset{CH_3}{^3CH}—^4CH_2—\underset{\underset{CH_3}{CH_2}}{^5CH}—^6CH_2—^7CH_3$$

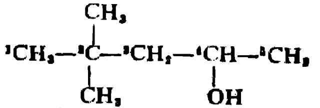
is 5-ethyl-2,3-dimethylheptane.

5. **Lowest Number for Functional Group.**—In case some functional group is present in the chain, the lowest number is to be assigned to it, even if the lowest number rule is violated. For example,



$$^5CH_3—\underset{CH_3}{\overset{CH_3}{^4C}}—^3CH_2—\underset{OH}{^2CH}—^1CH_3$$

4, 4-dimethyl-2-pentanol
Right



$$^1CH_3—\underset{CH_3}{\overset{CH_3}{^2C}}—^3CH_2—\underset{OH}{^4CH}—^5CH_3$$

2, 2-dimethyl-4-pentanol
Wrong

A double or triple bond is also regarded as a functional group. The lowest number is, however, given in the following order of preference :

(*i*) To the principal functional group of the compound.

(*ii*) To the double or triple bond.

(*iii*) To the substituents (atom or groups designated by prefixes).

In the event there are more than one functional groups in a molecule, the following order of preference is given in the choice of the principal functional group which is to be given the lowest number:

(1) acids
(2) acid derivatives (except nitrile)
(3) aldehydes
(4) nitriles
(5) ketones
(6) alcohols
(7) amines
(8) ethers
(9) olefins
(10) acetylenes

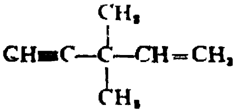
For example, the name for the allyl alcohol would be

$${}^3CH_2={}^2CH-{}^1CH_2OH$$

2-Propen-1-ol.

(Lowest number assigned to OH in preference to double bond.)

Similarly note the name of the compound given below:



$$CH\equiv C-C(CH_3)_2-CH=CH_2$$

3, 3-dimethyl-1-penten-4-yne

(Both double and triple bonds are at equal distances from chain ends. Numbering is, therefore, determined by double bond.)

For purposes of nomenclature, the halo-, nitroso-, and azo-groups are considered as substituents, not as functional groups. No endings, therefore, exist for them in the systematic nomenclature.

When two functional groups are present in the compound, one of them will be selected as the principal functional group following the order of preference as indicated before. The other functional group present will be secondary functional group and will be treated as a substituent. The prefixes and suffixes when various functional groups are used as substituents and functional groups are given in the following table along with the prefixes for the known substituents.

Table 9·1—Substitutive names of Functional Groups.

(*a*) **Groups cited only as Prefixes:**

$-Br$ Bromo	$-Cl$ Chloro	$-ClO$ Chlorosyl	$-ClO_2$ Chloryl	$-ClO_3$ Perchloryl
$-F$ Fluoro	$-I$ Iodo	$-N=C=O$ Carbonylamino	$-N=C=S$ Thiocarbonylamino	
$=N_2$ Diazo	$-N_3$ Azido	$-NC$ Carbylamino	NO Nitroso	$-NO_2$ Nitro
$=N(O)OH$ *aci*-Nitro		$-OC\equiv N$ Cyanato	$-OOH$ Hydroperoxy	$-OR$ R-oxy
$-OOR$ R-dioxy		$-S\equiv N$ Thiocyanato	$-SR$ R-thio	$-S(O)R$ R-sulphinyl
$-SO_2R$ R-sulphonyl		$-SSR$ R-dithio		

(*b*) **Groups cited as either Prefixes or Suffixes.**

Functional Group	*Prefix name*	*Suffix name*
$-\mathit{C}OOH$	—	-oic acid
$-COOH$	Carboxy	carboxylic acid
$-SO_2OH$	Sulpho	-sulphonic acid
$-\mathit{C}OX$	—	-oyl (-yl) halide
$-COX$	Haloformyl	-carbonyl halide
$-\mathit{C}ONH_2$	—	-amide
$-CONH_2$	Carbamoyl	-carboxamide
$-\mathit{C}\equiv N$	—	-nitrile
$-C\equiv N$	Cyano	-carbonitrile
$-\mathit{C}HO$	Oxo	-al
$-CHO$	Formyl	-carbaldehyde
$>C=O$	Oxo	-one
$>C=S$	Thioxo	-thione
$-OH$	Hydroxy	-ol
$-SH$	Mercapto	-thiol
$-NH_2$	Amino	-amine
$=NH$	Imino	-imine

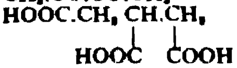
N B In the functional groups given above an italic *C* indicates that the carbon atom so designated is not included in the corresponding suffix or prefix name

6. Names of Compounds containing more than one functional groups.—In the case of compounds containing more than one functional groups, the ending is suitably modified. Carbon-carbon multiple bonds and a second function are combined in endings , otherwise the important functional group is handled as substituent. For example 2-Propen-1-ol given above and

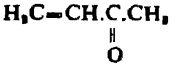
$CH_2=CH-CH=CH_2$	$CH_2OH-CHOH-CH_2OH$
1, 3 Butadiene	1, 2, 3-Propanetriol
(It is **diene** due to the presence of 2 double bonds)	(It is **triol** due to the presence of 3 OH groups.)

Names of certain compounds containing two or more simple or complex functions are given in the following tables :

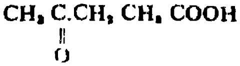
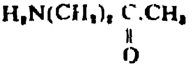
(a) Nomenclature of some Simple Polyfunctional Compounds.

Functional Groups	*Generic Name*	*Specific Example*	
		Structure	*Name*
(*i*) two hydroxyl	alkanediol	$HOCH_2.CH_2OH$	1, 2-ethanediol
(*ii*) three hydroxyl	alkanetriol	$HOCH_2.CH(OH)\ CH_2OH$	1, 2, 3-propanetriol
(*iii*) two double bonds	alkadiene	$H_2C=CH.CH=CH_2$	1, 3-butadiene
(*iv*) two acids	alkanedioic acid	$HOOC(CH_2)_3COOH$	pentanedioic acid
(*v*) two aldehydes	alkanedial	$O=HC(CH_2)_6CHO$	octanedial
(*vi*) two ketones	alkanedione	$CH_3.CO.CO.CH_3$	2,3-butanedione
(*vii*) three acids	tricarboxylic acid	 $\begin{matrix}HOOC.CH_2 & CH & .CH_2\\ & \vert & \vert\\ & HOOC & COOH\end{matrix}$	1, 2, 3-propane tricarboxylic acid

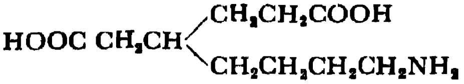
(b) Nomenclature of some Unsaturated Compounds of Simple Functions

Unsaturation and Functional group	*Generic Name*	*Specific Example*	
		Structure	*Name*
(*i*) double bond, acid	alkenoic acid	$CH_2=CH.COOH$	propenoic acid
(*ii*) triple bond, aldehyde	alkynal	$HC\equiv C.CHO$	propynal
(*iii*) double bond, ketone	alkenone	 $H_2C=CH.\underset{\underset{O}{\Vert}}{C}.CH_3$	3-buten-2-one
(*iv*) two double bonds, alcohol	alkadienol	$(CH_2=CH.CH_2)_2CHOH$	1, 6-heptadien-4-ol
(*v*) double bond, two hydroxyls	alkenediol	$HOCH_2\ CH=CH\ CH_2OH$	2-butene-1, 4-diol

(c) Nomenclature of some Compounds of Complex Functions

Class of Compound	*Generic Name*	*Specific Example*	
		Structure	*Name*
(*i*) keto acid	oxoalkanoic acid	 $CH_3\ \underset{\underset{O}{\Vert}}{C}.CH_2\ CH_2\ COOH$	4-oxopentanoic acid
(*ii*) hydroxy acid	hydroxyalkanoic acid	$HOCH_2.COOH$	hydroxyethanoic acid
(*iii*) amino acid	aminoalkanoic acid	$H_2N(CH_2)_5COOH$	6-aminohexanoic acid
(*iv*) cyano acid	cyanoalkanoic acid	$N\equiv C\ CH_2\ COOH$	cyanoethanoic acid
(*v*) aminoketone	aminoalkanone	 $H_2N(CH_2)_2\ \underset{\underset{O}{\Vert}}{C}.CH_3$	4-mino-2-butanone
(*vi*) alkoxyalcohol	alkoxyalkanol	$CH_3O.CH_2.CH_2OH$	2-methoxyethanol

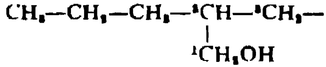
Treatment of "Like things Alike". All groups of one kind occurring in a single molecule should be given like treatment as far as possible. For example, in the compound,



The principal function is carboxylic acid, the parent compound should be so chosen as to include as many COOH groups as possible. Its name as 3-(4-Aminobutyl) hexanedioic acid is preferred to

8-Amino-4-(Carboxymethyl) octanoic acid.

7. **Functional groups and the chain selected.**—Maximum number of functional groups must be included in the carbon atoms chain selected, even if it does not satisfy the longest chain rule. If the longest chain does not include the maximum number of functional groups, the next longest chain which includes these should be selected. For example, while naming the compound

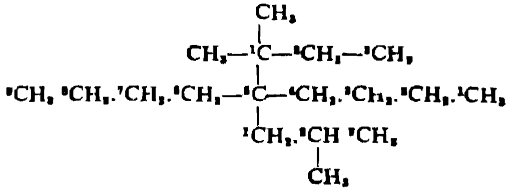


$$CH_3-CH_2-CH_2-{}^{2}\underset{\substack{|\\ {}^{1}CH_2OH}}{C}H-{}^{3}CH_2-{}^{4}CH_2-{}^{5}CH_3$$

2-Propyl-1-pentanol

we cannot select 7-carbon atom chain because it does not include the functional group. It has to be named as a derivative of 5-carbon atom chain.

Where there is a side-chain within a side-chain, the latter is numbered, and the name of the complex is considered to begin with the first letter of its complete name, *e.g.*,

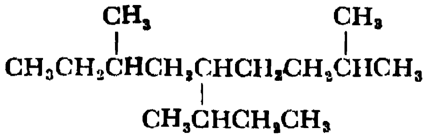


$${}^{9}CH_3\,{}^{8}CH_2.{}^{7}CH_2.{}^{6}CH_2-{}^{5}\overset{\substack{CH_3-{}^{1}\overset{\substack{CH_3\\|}}{C}-{}^{2}CH_2-{}^{3}CH_3\\|}}{\underset{\substack{|\\{}^{1}CH_2.{}^{2}\underset{\substack{|\\CH_3}}{C}H\,{}^{3}CH_3}}{C}}-{}^{4}CH_2.{}^{3}CH_2.{}^{2}CH_2.{}^{1}CH_3$$

is 5-(1, 1-dimethylpropyl)-5-(2-methylpropyl)-nonane.

or 5-isobutyl-5-*tert*-pentylnonane.

Similarly



$$CH_3CH_2\overset{\substack{CH_3\\|}}{C}HCH_2\underset{\substack{|\\CH_3CHCH_2CH_3}}{C}HCH_2CH_2\overset{\substack{CH_3\\|}}{C}HCH_3$$

is 5-*sec*-Butyl-2, 7-dimethylnonane

or 5-(1-methylpropyl)-2, 7-dimethylnonane

8. **Writing the IUPAC names.**—Writing of the IUPAC name of the compound with a given structural formula involves the following steps :

(*i*) *Locate the longest chain* containing the principal functional group and as many of the secondary functional groups and multiple bonds as possible.

(*ii*) *Select the root word* corresponding to the length of the chain. For example *pent* for a five C-atom chain and *oct* for an eight C-atom chain. In the case of alicyclic compounds add the prefix *cyclo* to the root word.

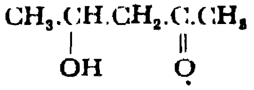
(*iii*) *Number the longest chain selected* from the end nearer to the principal functional group or substituents/side-chains in case there is no functional group.

(*iv*) Depending upon the nature of carbon-carbon bonds (C—C, C=C or C≡C), *attach the suffix* **-ane** (for C—C bonds), **ene** (for C=C bond) and **-yne** (for C≡C bond) to the root word.

(*v*) *Add suitable prefixes and suffixes* with numerals to indicate the number and position of each side chain, substituent or functional group.

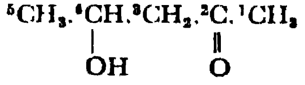
Some examples are given below to illustrate the above rules of nomenclature :

Example 1. *Name the compound whose molecular formula is given below :*



$$CH_3.\underset{\underset{OH}{|}}{CH}.CH_2.\underset{\underset{O}{\|}}{C}.CH_3$$

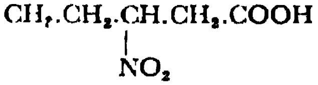
The longest chain contains five carbon atoms and no double or triple bond. It is, therefore, a derivative of pentane. There are two functional groups —OH and >C=O situated equidistant from the ends. But the latter stands higher in the order of preference. Hence numbering must start from right-hand side to give the lowest possible number to >CO.



$${}^5CH_3.{}^4\underset{\underset{OH}{|}}{CH}.{}^3CH_2.{}^2\underset{\underset{O}{\|}}{C}.{}^1CH_3$$

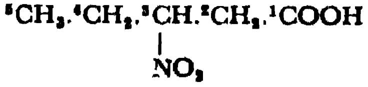
>CO being the principal functional group will be indicated (by the suffix *-one* while —OH being the secondary functional group will be treated as a substituent and indicated by a prefix ***hydroxy-*** . Its name, therefore, will be 4-hydroxy-2-pentanone.

Example 2. *Name the compound represented by the formula :*



$$CH_3.CH_2.\underset{\underset{NO_2}{|}}{CH}.CH_2.COOH$$

The longest chain contains five carbon atoms and it should be numbered from right-hand side to give the lowest number to the functional group —COOH.

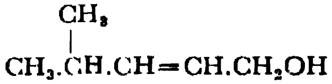


$${}^5CH_3.{}^4CH_2.{}^3\underset{\underset{NO_2}{|}}{CH}.{}^2CH_2.{}^1COOH$$

—COOH being the functional group will be indicated by the suffix *-oic acid* whereas the —NO_2 group being the substituent will be indicated by the prefix nitro- . Its name will, therefore, be

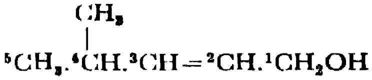
3-Nitro-1-pentanoic acid or 3-Nitropentanoic acid (Position of COOH group is understood to be 1).

Example 3. *Name the compound from its structural formula given below :*



$$\begin{array}{l}\qquad\quad CH_3 \\ \qquad\quad | \\ CH_3.CH.CH{=}CH.CH_2OH\end{array}$$

The longest chain contains five carbon atoms and a double bond. It is, therefore, a derivative of *pentene.* Numbering is to start from right-hand side nearest to the principal functional group.

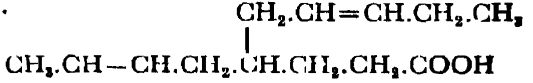


$$\begin{array}{l}\qquad\quad CH_3 \\ \qquad\quad | \\ {}^5CH_3.{}^4CH.{}^3CH{=}{}^2CH.{}^1CH_2OH\end{array}$$

—OH being the principal functional group will be indicated by the suffix -ol. Double bond will be indicated by the suffix *-ene* with the root word. Its name will, therefore, be

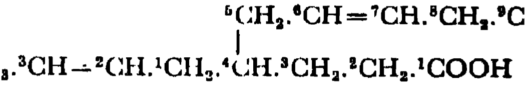
4-methyl-2-penten-1-ol

Example 4. *Write the IUPAC name of the compound with the following structural formula :*



$$\begin{array}{l}\qquad\qquad\qquad\qquad\qquad\quad CH_2.CH{=}CH.CH_2.CH_3 \\ \qquad\qquad\qquad\qquad\qquad\quad | \\ CH_3.CH{-}CH.CH_2.CH.CH_2.CH_2.COOH\end{array}$$

Although the longest chain contains 10 carbon atoms and two double bonds, but does not include the principal functional group, COOH. Hence we select the longest chain with nine carbon atoms which includes the COOH group and only one double bond. Numbering this chain from the end carrying COOH group and numbering the side chain, we get



$$\begin{array}{l}\qquad\qquad\qquad\qquad\qquad\quad {}^5CH_2.{}^6CH{=}{}^7CH.{}^8CH_2.{}^9CH_3 \\ \qquad\qquad\qquad\qquad\qquad\quad | \\ {}^4CH_3.{}^3CH{=}{}^2CH.{}^1CH_2.{}^4CH.{}^3CH_2.{}^2CH_2.{}^1COOH\end{array}$$

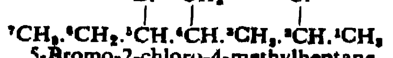
The side chain is an alkenyl group (2-Butenyl).

The longest chain contains 9 carbon atoms and one double bond, so it is a derivative of nonene. The principal functional group COOH will be indicated by the suffix *-oic acid.* Its name, therefore, is

4-(2-Butenyl)-6-nonenoic acid

After a little practice, these steps become only a mental exercise. We simply number the carbon atoms chain and write the name straight as given in the following examples :

(i)

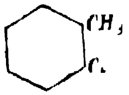


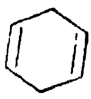
$$\begin{array}{l}\qquad\qquad\quad Br\;\; CH_3 \qquad\; Cl \\ \qquad\qquad\quad |\quad\;\; | \qquad\quad\; | \\ {}^7CH_3.{}^6CH_2.{}^5CH.{}^4CH.{}^3CH_2.{}^2CH.{}^1CH_3\end{array}$$

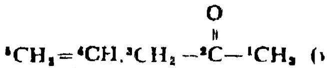
5-Bromo-2-chloro-4-methylheptane

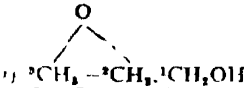
(Prefixes are arranged in the alphabetic order)

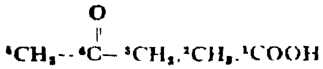
(*ii*) $^{6}CH_3{-}^{5}C{\equiv}^{4}C{-}^{3}CH{=}^{2}CH{-}^{1}CH_3$
2-Hexen-4-yn.

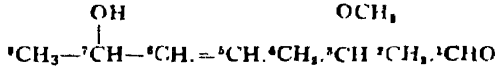
(*iii*)

1-Chloro-2-methylcyclohexane

(*iv*)

1, 4-Cyclohexadiene

(*v*)

$^{5}CH_2{=}^{4}CH.^{3}CH_2{-}^{2}\overset{O}{\overset{\|}{C}}{-}^{1}CH_3$
4-Penten-2-one

(*vi*)

2, 3-Epoxy-1-Propanol

(*vii*)

$^{5}CH_3{-}^{4}\overset{O}{\overset{\|}{C}}{-}^{3}CH_2.^{2}CH_2.^{1}COOH$
4-Oxopentanoic acid (Common name : γ-Ketovaleric acid)

(*viii*)

$^{8}CH_3{-}^{7}\overset{OH}{\overset{|}{C}}H{-}^{6}CH.{=}^{5}CH.^{4}CH_2.^{3}\overset{OCH_3}{C}H\ ^{2}CH_2.^{1}CHO$
7-Hydroxy-3-methoxy-5-octenal

9. Writing the structural formula from the given IUPAC name.— For writing the structural formula of the compound when its IUPAC name is given, we proceed as follows :

(*i*) *Locate the parent alkane* from the name and write the number of carbon atoms of this alkane in a straight chain and number them. Numbering may start from any end.

(*ii*) *Now locate the suffix* which gives information about the nature and number of the functional groups along with their positions.

(*iii*) *Lastly, locate the groups or/and substituents* mentioned in the prefix and the carbon atoms to which these are attached as indicated by the locants.

(*iv*) This gives us the skeleton formula. Now add hydrogen atoms to satisfy four valencies of each carbon atom to get the structural formula.

Thus for writing the structural formula of 3-Ethyl-2, 5-dimethyl-1, 4-heptadiene, we proceed as follows :

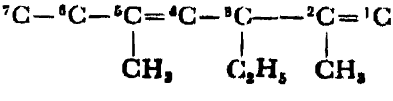
(*i*) Parent alkane of the compound is heptane. Write seven carbon atoms in a straight chain and number these.

$$^{7}C{-}^{6}C{-}^{5}C{-}^{4}C{-}^{3}C{-}^{2}C{-}^{1}C$$

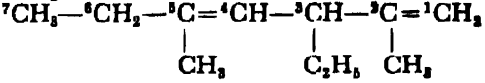
(*ii*) The suffix diene indicates two double bonds in 1 and 4 positions.

$$^{7}C{-}^{6}C{-}^{5}C{=}^{4}C{-}^{3}C{-}^{2}C{=}^{1}C$$

(*iii*) To locate the groups mentioned in the prefix, we attach one C_2H_5 to ^{3}C and two CH_3 groups to ^{2}C and ^{5}C to get


$$^{7}C{-}^{6}C{-}^{5}\underset{\underset{CH_3}{|}}{C}{=}^{4}C{-}^{3}\underset{\underset{C_2H_5}{|}}{C}{-\!-}^{2}\underset{\underset{CH_3}{|}}{C}{=}^{1}C$$

(*iv*) Finally adding H-atoms to satisfy four valencies of each carbon atom, we get



$$^{7}CH_3—^{6}CH_2—\underset{CH_3}{^{5}C}=^{4}CH—\underset{C_2H_5}{^{3}CH}—\underset{CH_3}{^{2}C}=^{1}CH_2$$

Similarly, to write the structural formula of the compound, 7-hydroxy-3-methoxy-4-methyl-5-heptenoic acid, we proceed as under :

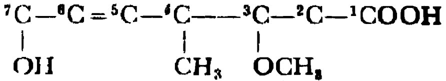
(*i*) Parent alkane of the compound is heptane. Write seven carbon atoms in a straight chain and number these

$$^{7}C—^{6}C—^{5}C—^{4}C—^{3}C—^{7}C—^{1}C$$

(*ii*) The suffix *enoic acid* indicates the presence of functional group—COOH at the end of the chain (position 1).

$$^{7}C—^{6}C—^{5}C—^{4}C—^{3}C—^{2}C—^{1}COOH$$

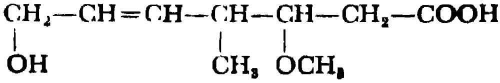
(*iii*) To locate the substituents mentioned in the prefix 7-hydroxy 3-methoxy-4-methyl, and the double bond indicated by 5-ene, we attach one OH group with ^{7}C, one OCH_3 group with ^{3}C, one CH_3 group with ^{4}C and a double bond between ^{5}C and ^{6}C. This gives



$$\underset{OH}{^{7}C}—^{6}C=^{5}C—\underset{CH_3}{^{4}C}——\underset{OCH_3}{^{3}C}—^{2}C—^{1}COOH$$

(*Skeleton formula*)

(*iv*) Finally adding H-atoms to satisfy four valencies of each carbon atom, we get the structural formula



$$\underset{OH}{CH_2}—CH=CH—\underset{CH_3}{CH}—\underset{OCH_3}{CH}—CH_2—COOH$$

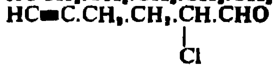
QUESTIONS

1. Write the structural formulae :

(*a*) 4-Ethyl-5-methyl-2-hexene.
(*b*) 3,5-Octadiene.
(*c*) 2-Chloro-3-methylbutane,
(*d*) 1,3-Diiodo-4-octene.
(*e*) 3-Buten-1-ol.
(*f*) 2-Aminoethanol.
(*g*) 1-Hydroxy-2-propanone
(*h*) 4-Oxopentanoic acid.
(*i*) 2-Nitropropanoic acid.

2. Name the following :

(*a*) $(CH_3)_2C=CH_2$.
(*b*) $(CH_3)_2CH.CH_2.CH(CH_3)_2$.
(*c*) $(CH_3)_2CH.CH_2.CH_2Cl$.
(*d*) $HOCH_2.CH_2.CH_2.CH_2.CH_2OH$
(*e*) $(CH_3)_3C.OH$.
(*f*)



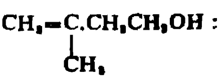
$$HC\equiv C.CH_2.CH_2.\underset{Cl}{CH}.CHO$$

(*g*) $(CH_3)_2CH.N(CH_3)_2$.
(*h*) $HOCH_2.CH=CH.CH_2OH$.
(*i*) $(CH_3)_2C=CH\ CH=CH.CH=C(CH_3)_2$.

3. (*a*) Give IUPAC names of the compounds whose formulae are given below :

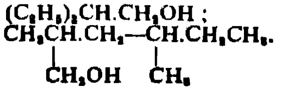
(*i*) $(C_2H_5)_2CH.CH_2OH$;

(*ii*)



$$CH_2=\underset{CH_3}{C}.CH_2CH_2OH :$$

(*iii*)



$$CH_3\underset{CH_2OH}{CH}.CH_2—\underset{CH_3}{CH}.CH_2CH_3.$$

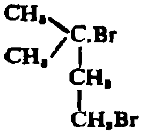
(*b*) Write structural formulae for the following compounds :
(*i*) 3-ethyl-2-methyl-1-hexene ; (*ii*) 2-methyl-2-penten-1-ol ;
(*iii*) 2, 4-Pentanedione.

4. Write Geneva names for the compounds whose formulae are given below :

(*i*) $(CH_3)_2CH.CH_2CH_3$; (*ii*) $(CH_3)_2CH.CH(CH_3)_2$;
(*iii*) $(C_6H_5)_2CH.CH_3$.

5. Give the structural formulae and Geneva names of the isomeric butyl alcohols.

6. Write Geneva names of the compounds whose formulae are given below :

(*i*) 

(*ii*) $CH_3.CH{=}CH.CH_2OH$;

(*iii*) $CH_2{=}CH.CH_2.CH_2OH$.

7. Write structural formulae of :

(*i*) 1, 2, 3-propanetriol ; (*ii*) 4-Methyl-2-pentene ;
(*iii*) 1, 4-diphenyl-1,3-butadiene.

8. Close this book and write under the structural formulae you have written in Q. 1, 3 (*b*) and 7, the IUPAC name for each compound. After completing the whole list compare your answers with those given. If there are differences, check the structure as well as the name to see where the error arose.

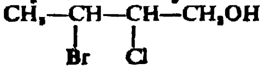
9. In a similar manner write structural formulae for the names you have written in Q. 2, 3(*a*), 4 and 6.

10. Are the following names correct in the IUPAC system of nomenclature ? If not, give the correct names.

(*a*) 3-pentyne (*b*) 4, 4, 3-trimethyl-1-hexyne
(*c*) 1, 6-hexadiene (*d*) octanediol
(*e*) *tert*. butanol (*f*) 2-keto-*n*-propanol.

11. Give IUPAC names of the following compounds :

(*i*) $CH_3{-}C{\equiv}C{-}CH_3$ (*ii*) $CH_2{=}CH{-}CH{=}CH_2$

(*iii*) 

$CH_3{-}\underset{Br}{CH}{-}\underset{Cl}{CH}{-}CH_2OH$

(*iv*) H—CHO

(*Delhi B.Sc. 1976*)

12. (*a*) Give the names of the following compounds according to IUPAC system of nomenclature :

(*i*) $CH_2{=}CH{-}CO{-}CH_2{-}CH_3$ (*ii*) $(CH_3)_3C{-}OH$

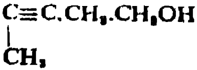
(*b*) Write the structures of the following compounds whose IUPAC names are given as under :

(*i*) 1, 5-hexadiene (*ii*) 4-Methyl-2-pentyne

(*Delhi B.Sc. Hons. 1976*)

13. Write the IUPAC names of the compounds having the following structural formulae :

(*i*) $(CH_3)_2C{=}CH_2$

(*ii*) 

$\underset{CH_3}{C}{\equiv}C.CH_2.CH_2OH$

(*iii*) $CH_2OH.CHOH.CH_2OH$
(*iv*) $(CH_3)_2CH.CH_2.OCH_3$

(*Delhi B.Sc. 1976 Supp.*)

14. Write structural formulae of the following compounds :

(*i*) 2, 4-hexadiene (*ii*) ethylmethylacetylene
(*iii*) [illegible]-pentanone (*iv*) butanal.

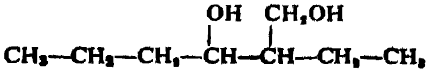
(*Delhi B.Sc. 1976 Supp.*)

15. (*a*) Write structures of the following compounds :

(*i*) 4-hydroxy-3-pentenoic acid

(*ii*) 6-ethyl-2-methyl-4-isopropyl-2-octene

(*b*) Write systematic (IUPAC) names for the following compounds :

(*i*) 

$CH_3{-}CH_2{-}CH_2{-}\overset{OH}{CH}{-}\overset{CH_2OH}{CH}{-}CH_2{-}CH_3$

(*ii*) $CH_3{-}CH_2{-}CH(Cl){-}CH_2{-}CHO$ (*Delhi B.Sc. 1977*)

16. Give the IUPAC names of the following compounds :

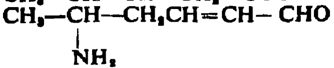
(*i*) $(CH_3)_2C(OH)—CH_2—CH(OH)—CH_3$

(*ii*) $(CH_3)_2CH—CH{=}CH—C{\equiv}CH$

(*iii*) $CH_3-CH(CH_3)-C(CH_3)(OH)-CH_2CH_3$

(*iv*) $CH_3—CH{=}CH—CH_2—COOH$

(*v*)

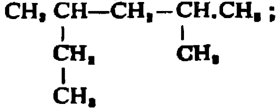


$CH_3—\underset{\displaystyle NH_2}{\underset{|}{CH}}—CH_2CH{=}CH—CHO$

(*vi*) $CH{\equiv}C—C(CH_3)_2—CH{=}CH_2$ (*Delhi B.Sc. Hons. 1980, 77*)

17. (*a*) Name the following compounds on IUPAC system :

(*i*) $CH_2OH-CHOH—CH_2OH$; (*ii*)



$CH_3\,\underset{\underset{\displaystyle CH_3}{\underset{|}{CH_2}}}{\underset{|}{CH}}—CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}.CH_3$;

(*iii*) $CH_2{=}CH-CH_2—CH_2OH$; (*iv*) $CH_3CH{=}CH\,CH_2CH_2OH.$

(*b*) Draw the structures

(*i*) 2,3-Dimethylbutane , (*ii*) 1, 3-Butadiene ;

(*iii*) Propane-1,2,3-tricarboxylic acid ,

(*iv*) 3-Buten-1-ol (*Jammu B.Sc. 1975*)

18. Write the structural formulae for the following compounds :

(*i*) 4-pentyn-1-ol. (*ii*) 3-ethyl-5-hydroxy-3-hexenal.

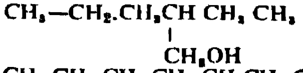
(*iii*) 3, 5-octadiene (*iv*) 4-cyano-4-ethyl-3-heptanone.

(*v*) 4-hydroxy-3-pentenoic acid (*vi*) 2, 3-pentanedione.

(*Delhi B Sc Hons 1980 ; Guru Nanak Dev B.Sc 1977*)

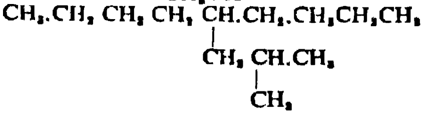
19. (*a*) Name the following by IUPAC system :

(*i*)



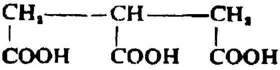
$CH_3—CH_2.CH_2\underset{\displaystyle CH_2OH}{\underset{|}{CH}}\,CH_2\,CH_3$

(*ii*)



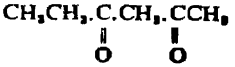
$CH_3.CH_2\,CH_2\,CH_2\,\underset{\displaystyle CH_2\,\underset{\underset{\displaystyle CH_3}{|}}{CH}.CH_3}{\underset{|}{CH}}.CH_2.CH_2CH_2CH_3$

(*iii*)



$\underset{\displaystyle COOH}{\underset{|}{CH_2}}——\underset{\displaystyle COOH}{\underset{|}{CH}}——\underset{\displaystyle COOH}{\underset{|}{CH_2}}$

(*iv*)



$CH_3CH_2.\underset{\displaystyle O}{\underset{\|}{C}}.CH_2.\underset{\displaystyle O}{\underset{\|}{C}}CH_3$

(*b*) Draw the structures :

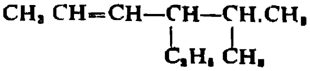
(*i*) 1, 2, 3-Propanetriol ; (*ii*) 3-Butene-1,2-diol ;

(*iii*) 2, 3-Diiodo-4-octene ; (*iv*) 3-ethyl-2-methyl-1-hexene.

(*Jammu B.Sc. 1977*)

ANSWERS

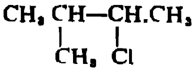
1. (*a*)



$CH_3\,CH{=}CH—\underset{\displaystyle C_2H_5}{\underset{|}{CH}}—\underset{\displaystyle CH_3}{\underset{|}{CH}}.CH_3$

(*b*) $CH_3.CH_2\,CH{=}CH.CH{=}CH.CH_2.CH_3$

(*c*)

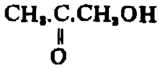


$CH_3\,\underset{\displaystyle CH_3}{\underset{|}{CH}}—\underset{\displaystyle Cl}{\underset{|}{CH}}.CH_3$

(*d*) $CH_3\,CH_2\,CH_2\,CH{=}CH.CHI.CH_2.CH_2I$

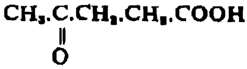
(*e*) $HO.CH_2\,CH_2.CH{=}CH_2$ (*f*) $H_2N.CH_2.CH_2.OH$

(*g*)



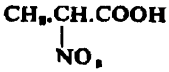
$CH_3.\underset{\displaystyle O}{\underset{\|}{C}}.CH_2OH$

(*h*)



$CH_3.\underset{\displaystyle O}{\underset{\|}{C}}.CH_2.CH_2.COOH$

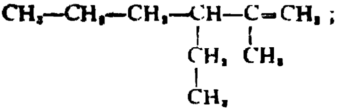
(*i*)



$CH_3.\underset{\displaystyle NO_2}{\underset{|}{CH}}.COOH$

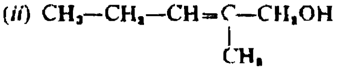
2. (*a*) 2-Methyl-1-propene. (*b*) 2, 4-Dimethylpentane.
(*c*) 1-Chloro-3-methylbutane. (*d*) 1, 5-Pentanediol.
(*e*) 2-Methyl-2-propanol. (*f*) 2-Chloro-5-hexyn-1-al.
(*g*) *N*, *N*-dimethyl-2-propanamine. (*h*) 2-butene-1, 4-diol.
(*i*) 2, 7-dimethyl-2, 4, 6-octatriene.

3. (*a*) (*i*) 2-ethyl-1-butanol ; (*ii*) 3-methyl-3-buten-1-ol ;
(*iii*) 2, 4-dimethyl-1-hexanol
(*b*) (*i*)



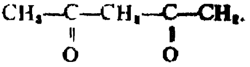
$$CH_3{-}CH_2{-}CH_2{-}\underset{\underset{CH_3}{|}{\underset{CH_2}{|}}}{CH}{-}\underset{\underset{CH_3}{|}}{C}{=}CH_2\ ;$$

(*ii*)



$$CH_3{-}CH_2{-}CH{=}\underset{\underset{CH_3}{|}}{C}{-}CH_2OH\ ;$$

(*iii*)

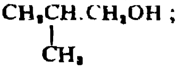


$$CH_3{-}\underset{\underset{O}{\|}}{C}{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}CH_3.$$

4. (*i*) 2-methylbutane ; (*ii*) 2, 3-dimethylbutane ;
(*iii*) 3-methylpentane.

5. (*i*) $CH_3.CH_2.CH_2.CH_2OH$; 1-Butanol (*ii*) $CH_3\ CH_2CHOH.CH_3$; 2-Butanol

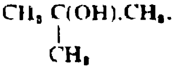
(*iii*)



$$\underset{\underset{CH_3}{|}}{CH_3CH}.CH_2OH\ ;$$

2-methyl-1-propanol

(*iv*)

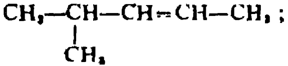


$$CH_3\ \underset{\underset{CH_3}{|}}{C}(OH).CH_3.$$

2-methyl-2-propanol

6. (*i*) 1 ,3-dibromo-3-methylbutane ; (*ii*) 2-Penten-1-ol ;
(*iii*) 3-Buten-1-ol.

7. (*i*) $CH_2OH{-}CHOH{-}CH_2OH$;
(*ii*)



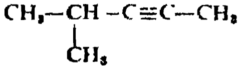
$$CH_3{-}\underset{\underset{CH_3}{|}}{CH}{-}CH{=}CH{-}CH_3\ ;$$

(*iii*) $C_6H_5{-}CH{=}CH{-}CH{=}CH{-}C_6H_5$.

10. (*a*) No, it should be 2-pentyne.
(*b*) No, it should be 3, 4, 4-trimethyl-1-hexyne.
(*c*) No, it should be 1, 5-hexadiene.
(*d*) No, positions of two OH groups must be indicated by numbers, (1, 8- or 1, 7-, etc.).
(*e*) No, use of *tert*. in IUPAC system is not allowed. It is 2-methyl-2-propanol.
(*f*) No, use of *n* in IUPAC system is not allowed. Moreover keto is the principal function and should form suffix. It is 1-hydroxy-2-propanone
(*g*) No, it should be 1-Hydroxy-2-propanone.

11. (*i*) 2-Butyne (*ii*) 1, 3-Butadiene
(*iii*) 3-Bromo-2-chloro-1-butanol (*iv*) Methanal.

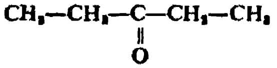
12. (*a*) (*i*) 1-Penten-3 one. (*ii*) 2-Methyl-2-propanol.
(*b*) (*i*) $CH_2{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2$
(*ii*)



$$CH_3{-}\underset{\underset{CH_3}{|}}{CH}{-}C{\equiv}C{-}CH_3$$

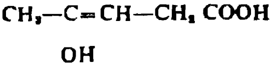
13. (*i*) 2-Methyl-1-propene (*ii*) 3-Pentyn-1-ol
(*iii*) 1, 2, 3-Propanetriol (*iv*) 1-Methoxy-2-methylpropane

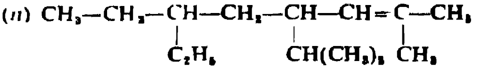
14. (*i*) $CH_3{-}CH{=}CH{-}CH{=}CH{-}CH_3$ (*ii*) $CH_3{-}CH_2{-}C{\equiv}C{-}CH_3$.
(*iii*)



$$CH_3{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}CH_2{-}CH_3$$

(*iv*) $CH_3.CH_2.CH_2.CHO$.

15 (*a*) (*i*) 
$CH_3—\underset{OH}{C}=CH—CH_2\,COOH$

(*ii*) 
$CH_3—CH_2—\underset{C_2H_5}{CH}—CH_2—\underset{CH(CH_3)_2}{CH}—CH=\underset{CH_3}{C}—CH_3$

(*b*) (*i*) 2-Ethyl 1, 3-hexanediol (*ii*) 3-chloro-1-pentanal

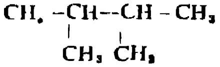
16 (*i*) 2 Methyl 2, 4-pentanediol (*ii*) 5-Methyl-3 hexen-1-yne

(*iii*) 2, 3-Dimethyl-3-pentanol (*iv*) 3-Pentenoic acid

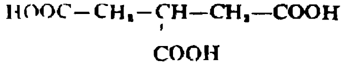
(*v*) 5-Amino-2-hexen-1-al (*vi*) 3, 3-Dimethyl-1-penten-4-yne

17 (*a*) (*i*) 1, 2, 3 propanetriol (*ii*) 2, 4-Dimethylhexane

(*iii*) 3-Buten-1-ol (*iv*) 3-Penten-1-ol.

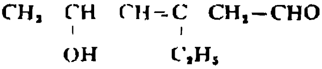
(*b*) (*i*) 
$CH_3—\underset{CH_3}{CH}—\underset{CH_3}{CH}—CH_3$

(*ii*) $CH_2=CH—CH=CH_2$

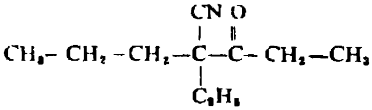
(*iii*) 
$HOOC—CH_2—\underset{COOH}{CH}—CH_2—COOH$

(*iv*) $CH_2—CH—CH_2—CH_2OH$

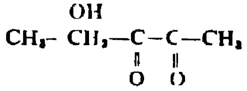
18 (*i*) $CH\equiv C—CH_2—CH_2—CH_2OH$

(*ii*) 
$CH_3—\underset{OH}{CH}—CH=\underset{C_2H_5}{C}—CH_2—CHO$

(*iii*) $CH_3—CH_2—CH=CH—CH=CH—CH_2—CH_3$

(*iv*) 
$CH_3—CH_2—CH_2—\overset{CN}{\underset{C_2H_5}{C}}—\overset{O}{\overset{\|}{C}}—CH_2—CH_3$

(*v*) $CH_3—C=CH—CH_2—COOH$

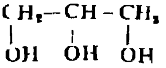
(*vi*) 
$CH_3—\overset{OH}{CH_2}—\underset{O}{\underset{\|}{C}}—\underset{O}{\underset{\|}{C}}—CH_3$

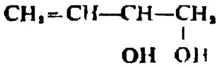
19. (*a*) (*i*) 2-Ethyl-1-pentanol

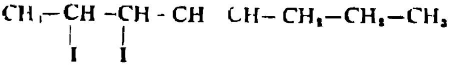
(*ii*) 5-(2-methylpropyl)-nonane or 5-Isobutylnonane

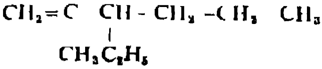
(*iii*) 1, 2, 3-Propanetricarboxylic acid.

(*iv*) 2 4-Hexanedione

(*b*) (*i*) 
$\underset{OH}{CH_2}—\underset{OH}{CH}—\underset{OH}{CH_2}$

(*ii*) 
$CH_2=CH—\underset{OH}{CH}—\underset{OH}{CH_2}$

(*iii*) 
$CH_3—\underset{I}{CH}—\underset{I}{CH}—CH=CH—CH_2—CH_2—CH_3$

(*iv*) 
$CH_2=C\quad\underset{CH_3C_2H_5}{CH}—CH_2—CH_3\quad CH_3$

10

The General Nature of Organic Reactions

1. Introduction.—A chemical equation indicates the reactants and the final products of the reaction. It rarely indicates *how* the reaction proceeds. Much work has recently been done on *the reaction mechanism, i.e., the actual steps in which a chemical reaction occurs.* The chief advantage of the mechanistic approach to organic chemistry lies in the fact that with the help of a relatively smaller number of guiding principles we can explain how a reaction proceeds and even forecast the outcome of changing the conditions of a certain chemical reaction.

2. The Breaking and Forming of Bonds.—Let us examine what happens when a molecule R—L containing a covalent bond undergoes chemical reaction with an attacking reagent A to give A—R another covalent compound.

$$A + R{-}L \rightarrow A{-}R + L$$

In this reaction the covalent bond R—L has been broken and the new bond A—R has been formed. There are three possible ways in which breaking of the bond (**Bond Fission**) may take place depending upon the experimental conditions and nature of R, the attacking reagent A and the leaving group L

(*i*) Each atom (forming the R—L bond) retains the electrons of the shared pair, forming highly reactive entities called *free radicals* (or simply *radicals*) or *odd electron molecules*, *e.g.*, methyl radical, $CH_3^{\cdot}$, ethyl radical, $C_2H_5^{\cdot}$, etc.

$$R{-}L \rightarrow R^{\cdot} + L^{\cdot}$$

The breaking of the covalent bond in this manner is known as *homolytic fission or homolysis.*

(*ii*) The group R or L retains the shared pair of electrons.

$$\overset{\curvearrowleft}{R{-}L} \rightarrow \overset{-}{R}: + \overset{+}{L} \quad \text{or} \quad \overset{\curvearrowright}{R{-}L} \rightarrow \overset{+}{R} + :\overset{-}{L}$$

Breaking of the bond in this manner is known as *heterolytic fission or heterolysis.* When $\overset{-}{R}$: is a negative group in which the carbon atom carries the unshared pair of electrons, it is known as a **carbanion.** Carbanions appear to be capable of leading a separate existence. When $\overset{+}{R}$ is a positive group in which the carbon atom carries the positive charge, *i.e.*, lacks a pair of electrons, it is known

as a carbonium ion* or carbocation.

3. **Types of Organic Reactions.** Depending upon the type of bond fission involved, the organic reactions can be classified into two main categories :

(*a*) *Heterolytic reactions* which involve a heterolytic fission of the bond resulting in the formation of a carbanion or a carbonium ion as an intermediate.

(*b*) *Homolytic reactions* which involve a homolytic fission of the bond resulting in the formation of a free radical as an intermediate.

Depending upon the nature of the reaction which the intermediate species (carbanion, carbocation or free radical) undergoes, various types of reactions which we come across are :

(1) **Substitution.** These reactions involve the direct replacement of an atom/group by some other atom/group. For example,

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl \qquad ...(i)$$

$$CH_3Br + OH^- \rightarrow CH_3OH + Br \qquad (ii)$$

In (*i*) one hydrogen atom of CH_4 has been replaced by one chlorine atom In (*ii*) the bromine atom has been replaced by hydroxyl group

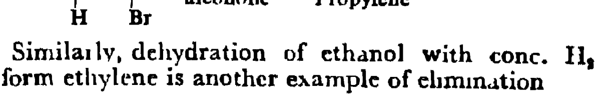
(2) **Addition.** *Addition reactions are those reactions in which one molecule is simply added to another molecule.* For example, (*i*) reaction between ethylene and bromine is an addition reaction.

$$CH_2{=}CH_2 + Br_2 \rightarrow CH_2Br - CH_2Br$$

(*ii*) Similarly, reaction between propylene and HI to form isopropyl iodide is another example of an addition reaction.

$$\underset{\text{Propylene}}{CH_3-CH{=}CH_2} + H-I \rightarrow \underset{\text{Isopropyl iodide}}{CH_3-CHI-CH_3}$$

(3) **Elimination.** *Elimination reactions are those in which two atoms or groups are removed from a molecule without being replaced by other atoms or groups.* For example, (*i*) Reaction between propyl bromide and alcoholic potash resulting in the removal of a molecule of hydrogen bromide is an *elimination reaction.*



$$CH_3-\underset{H}{\underset{|}{CH}}-\underset{Br}{\underset{|}{CH_2}} + \underset{\text{alcoholic}}{KOH} \rightarrow \underset{\text{Propylene}}{CH_3CH{=}CH_2} + KBr + H_2O$$

(*ii*) Similarly, dehydration of ethanol with conc. H_2SO_4 at 430K to form ethylene is another example of elimination

$$\underset{\text{Ethanol}}{CH_3-CH_2OH} + [H_2SO_4] \xrightarrow{430K} \underset{\text{Ethylene}}{CH_2{=}CH_2} + H_2O + [H_2SO_4]$$

(4) **Rearrangement.** In some of the organic molecules the functional group changes its position during the course of the

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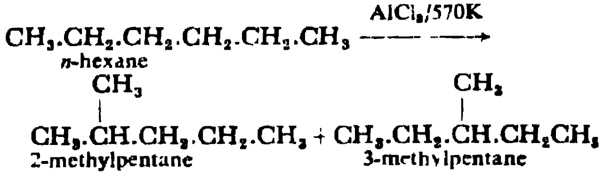
*The term *carbonium* in naming organic structures containing a positively charged carbon atom has been used very frequently The practice has been inconsistent and often confusing. The Nomenclature Committee of the American Chemical Society recommended (1973) that *carbonium* should no longer be used either as class name, *e.g* , 'carbonium ions' or in names of individual cations, *e.g.*, 'trimethylcarbonium' $[(CH_3)_3C^+]$ The class name *carbocations* (*t*-Butyl cation) and the systematic name *trimethylcarbenium* are preferred.

Carbenium is CH_3^+ obtained by addition of H^+ to H_2C : (*carbene*) reaction. Such a **reshuffling** of the molecule is termed **rearrangement**. For example,

(*i*) *n*-Alkanes when heated with $AlCl_3$ at 570K undergo rearrangement to give branched-chain alkanes.



$$CH_3.CH_2.CH_2.CH_2.CH_2.CH_3 \xrightarrow{AlCl_3/570K}$$

n-hexane

$$CH_3.\overset{\overset{CH_3}{|}}{C}H.CH_2.CH_2.CH_3 + CH_3.CH_2.\overset{\overset{CH_3}{|}}{C}H.CH_2CH_3$$

2-methylpentane 3-methylpentane

(*ii*) Alkyl halides when heated at about 570K or at a lower temperature in the presence of $AlCl_3$ as catalyst undergo rearrangement, *e.g.*, 1-bromobutane gives 2-bromobutane.

$$\underset{\text{1-bromobutane}}{CH_3.CH_2.CH_2.CH_2Br} \xrightarrow[AlCl_3]{570K} \underset{\text{2-bromobutane}}{CH_3.CH_2.CHBr.CH_3}$$

(3) **Polymerisation**. Union of two or more molecules to form a large single molecule is termed polymerisation. For example,

(*i*) Ethylene polymerises in presence of a suitable catalyst to give polyethylene.

$$n\,\underset{\text{Ethylene}}{CH_2{=}CH_2} \longrightarrow \underset{\text{Polyethylene}}{(-CH_2-CH_2-)_n}$$

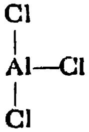
(*ii*) Acetylene on passing through a dull red hot tube polymerises to give benzene.

$$3\,\underset{\text{acetylene}}{CH{\equiv}CH} \longrightarrow \underset{\text{benzene}}{C_6H_6}$$

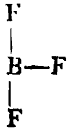
4. Heterolytic Reactions.—The heterolytic fission or heterolysis yields a carbocation or a carbanion. Heterolysis occurs due to the partial ionic character of the covalent bond in polar compounds. Mechanisms involving heterolytic fission during reactions are termed **ionic or polar mechanisms.**

As explained earlier the heterolytic reactions involve carbanions or carbocations as intermediates. Since these are charged intermediates, they will be preferentially attacked by electron-rich or electron-deficient reagents. Electron-deficient reagents which attack the negatively charged carbanions or the negatively charged centres in the molecules are termed **electrophiles** or **electrophilic reagents.** Electron-rich species which attack a carbocation or positively charged centres (or points of low electron density) are called **nucleophiles or nucleophilic reagents.**

Thus, electrophiles can be positively charged reagents or have vacant orbitals which can accept a lone pair of electrons, *e.g.*,



$$\begin{array}{l} Cl \\ | \\ Al—Cl \\ | \\ Cl \end{array}$$

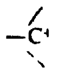


$$\begin{array}{l} F \\ | \\ B—F \\ | \\ F \end{array}$$

Both Al and B have a vacant orbital and can accept a lone pair of electrons.

Some common electrophiles are given in Table 10·1.

Table 10·1—Some Common Electrophiles

Positively Charged	Neutral
H^+ (*proton*)	$AlCl_3$
Cl^+ (*chloronium ion*)	BF_3
Br^+ (*bromonium ion*)	$ZnCl_2$
NO_2^+ (*nitronium ion*)	SO_3
NO^+ (*nitrosonium ion*)	$RCOCl$
 (*carbocation*)	
H_3O^+ (*Hydronium ion*)	

Similarly, nucleophiles can be negatively charged reagents or neutral species containing a lone pair of electron to be **donated** to electron-deficient molecules. Some of the common **nucleophiles are** given in Table 10·2.

Table 10·2—Some Common Nucleophiles

Negatively Charged		Neutral
X^-	(Halide ion = Cl, $\bar{\mathrm{Br}}$, I)	$\cdot NH_3$
$\bar{O}H$	(hydroxide ion)	$:OH_2$
$\bar{O}R$	(alkoxide ion)	$H-\overset{\cdot}{\underset{\cdot\cdot}{O}}-R$
$\bar{C}N$	(cyanide ion)	$R_3N:$
$\equiv\bar{C}:$	(carbanion)	$R-\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}-H$
$CH\equiv\bar{C}:$	(acetylide ion)	$R_2\underset{\cdot\cdot}{S}:$

5. Energetics of Ionic or Polar Mechanisms.—Chemical reaction between R—L and A (*attacking reagent*) to form A—R and L (*leaving group*) involves breaking of the R—L bond in any of the three ways discussed before and formation of a new bond between A and R. It does not, however, necessarily mean that bond fission occurs first and combination of R with A occurs afterwards. *One necessary condition for a chemical reaction is that a molecule must be activated before it enters into chemical reaction.*

We can expect that when various paths are possible for a given reaction under different conditions, then the path actually followed will be the one in which the lowest energy of activation is required. The transition state theory does not use the simple idea of collision but considers how the potential energy of the system of atoms and/or molecules changes as the molecules are brought together. Consider the *three-centre reaction*

$$A+BC \longrightarrow AB+C$$

Energy required is minimum when the reaction proceeds by an *end-on approach, i.e.*, when A approaches BC along the bonding line of BC and from the side remote from C (departing entity).

$$A\ldots\ldots\rightarrow\ldots\ldots B\text{—}C \longrightarrow A\text{—}B + C$$

In such a reaction the value of the activation energy *E* depends on four factors :

(*i*) The strength of the B—C bond. *E* is directly proportional to the strength of the bond.

(*ii*) The repulsion between A and BC. *E* is directly proportional to this repulsion.

(*iii*) The repulsion between AB and C. *E* is directly proportional to this repulsion.

(*iv*) The strength of A—B bond. *E* is inversely proportional to this bond strength.

Another factor which affects the value of *E* is solvation of molecules and ions since most reactions are carried out in solution.

While considering the mechanism of activation of such a reaction we can imagine two possible extreme cases :

(*i*) A is forced up against the repulsion of BC until it is close enough to compete for B on equal terms with C, which is finally expelled.

(*ii*) BC acquires so much energy that the bond B—C is broken, and then A and C combine without any opposition.

According to London and Polanyi, the lowest value of *E* is obtained when the reaction proceeds through a compromise between the above two extremes, *i.e.*, when A approaches BC along the bond-line of BC remote from C and is forced against repulsion of BC the bond BC stretches at the same time until A and C can compete for B on equal terms. *Thus a point is reached when the distances* A—B *and* B—C *are such that the forces between each pair are the same. In this state neither of the molecules* AB *and* BC *exists independently and the system can now proceed in either direction to form* A *and* BC *or* AB *and* C. *This condition is the* **transition state** (T.S.) *or* **activated complex.**

$$A + B\text{—}C \longrightarrow \underset{\text{T.S.}}{A\ldots\ldots B\ldots\ldots C} \longrightarrow A\text{—}B + C$$

It should be noted that the *new* bond is formed on the side opposite to that of the original bond which gets broken and the original molecule is turned '*inside out*', *i.e.*, *inverted*, when the new molecule is formed.

The sequence of events given above may be graphically represented by means of energy profile diagrams (Fig. 10·1 and 10·2). The horizontal coordinate in these diagrams, often called the reaction coordinate, need have no exact quantitative significance and merely represents the sequence of the reaction from reactants on the left to products on the right. The rate of the reaction is the rate at which reactant molecules pass through the transition state.

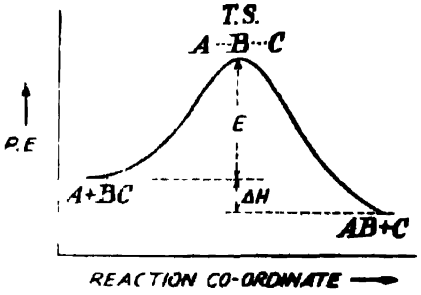


Fig. 10·1—Energy profile of an exothermic reaction.

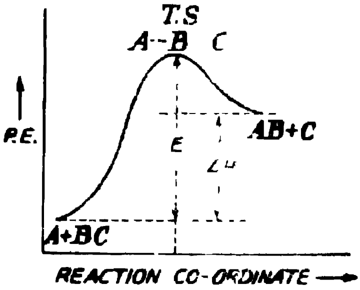


Fig. 10·2—Energy profile of an endothermic reaction.

In these diagrams ΔH is the heat of reaction at constant pressure and E is energy of activation. Lower the hump in the curve, lower is the energy barrier* and easier it is for the reactants to enter the transition state. Also the wider the hump for a given height, the easier it is for the reactants to enter the transition state owing to the wider latitude in the nuclei positions for the activated complex.

The activated complex contains partial bonds and the energy content of the system is maximum ; it is not a true molecule. Its life is extremely short, and hence it cannot be isolated ; it is always decomposing into the reactants and products. A complex reaction, however, proceeds through a true intermediate which, if stable enough, may be isolated. Fig. 10·3 depicts a reaction which proceeds through a true intermediate (I) shown by a minimum in the energy profile diagram The greater the dip, the more stable will be the intermediate. Conversely, the shallower the dip, the less stable will be the intermediate and in the extreme case it may be so shallow that the intermediate cannot be distinguished from the transition state.

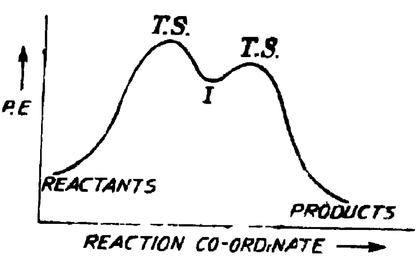


Fig. 10·3 —Energy profile diagram of reaction which proceeds through a true intermediate.

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* An analogy may be helpful here. Water seeks the position of minimum energy—it flows downhill. If you connect two basins of water at different heights, water flows from the higher to the lower level. If there is a barrier between the basins, they may be connected with a siphon, provided the barrier is not too high water will flow through the siphon over the barrier. When using the phrases like *the energy barrier* and *the reaction goes downhill to products*, chemists have this analogy in mind.

Kinetic *versus* **Thermodynamic Control**. Let us consider energy diagrams (Fig. 10·4) of two reactions A→B and A→C. Activation energy required for the conversion A→C being less, product C will form comparatively faster. Hence C is termed the ***kinetic product***.

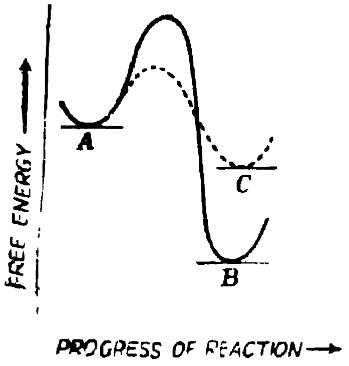


Fig. 10·4—Energy diagrams for the two reactions A→B and A→C.

However, B being associated with less free energy, is more stable. Hence if the reaction is allowed to proceed for a sufficiently long time, C will revert back to A which will slowly change to B. Under these circumstances, the three species A, B and C will be in equilibrium and the relative amounts of B and C will depend on their relative stabilities. B being more stable will be the predominating ***thermodynamic product***.

Thus we find that mild temperature and short reaction time favour the formation of kinetic product C whereas higher temperature and longer reaction time will favour the formation of thermodynamic product B.

In some cases when the more stable product may also have the smaller activation energy, the kinetic and thermodynamic products are identical.

Reaction Kinetics. According to the law of mass action, ***the rate of a chemical reaction is proportional to the product of the active masses of the reacting substances***. The molar concentration of A is generally taken as the active mass of A and represented by [A]. The equation relating reaction rate and the molar concentration is called ***rate law***. Suppose in a reaction

$$A+B \longrightarrow C+D$$

it is found experimentally that the rate was proportional to the concentration of A and to the square of the concentration of B, the rate law would be written as

$$\text{rate} = k\,[A]\,[B]^2$$

The constant *k* is the *rate constant* or *specific rate* and has a definite value at a definite temperature.

The sum of the exponents of the concentrations is the ***order of the reaction***. The above reaction is first order with respect to A, second order with respect to B, the reaction itself being a third order reaction. If in a certain case it is found that in the above reaction

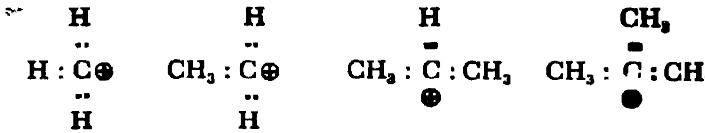
$$\text{rate} = k[B]^2$$

the reaction is ***zero order*** with respect to A.

When a reaction occurs via a number of steps, the slowest step determines the rate of the overall reaction*, provided the other steps are relatively rapid.

A number of reactions involve activated complex as explained above. Many of the organic ionic reactions may, however, be promoted by electrophilic and nucleophilic reagents.

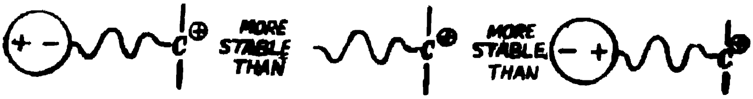
6. Carbocations.—To account for a wide variety of observations like dehydration of alcohols, dehydrohalogenation of alkyl halides, etc., the existence of a kind of reactive particle, the **carbocation** has been proposed. It is a *group of atoms that contains a carbon atom bearing only six electrons.* Carbocations are classified as primary, secondary or tertiary after the nature of the carbon atom bearing the positive charge. For example,



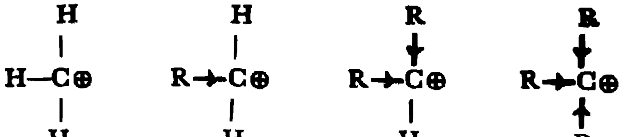
$$\begin{array}{cccc} \text{H} & \text{H} & \text{H} & \text{CH}_3 \\ \text{H}:\overset{..}{\underset{..}{\text{C}}}\oplus & \text{CH}_3:\overset{..}{\underset{..}{\text{C}}}\oplus & \text{CH}_3:\overset{..}{\text{C}}:\text{CH}_3 & \text{CH}_3:\overset{..}{\text{C}}:\text{CH}_3 \\ \text{H} & \text{H} & \oplus & \oplus \end{array}$$

Methyl cation | Ethyl cation (*primary*, *1°*) | Isopropyl cation (*secondary*, *2°*) | *tert*-Butyl cation (*tertiary*, *3°*)

Stability of Carbocations. *The stability of a charged system is increased by dispersal of the charge.* Any factor, therefore, that tends to spread out the positive charge of the electron-deficient carbon and distribute it over the rest of the ion must stabilize a carbocation. Thus these are stabilized inductively by electron-donating substituents and rendered less stable by electron-withdrawing substituents.



The alkyl group attached to the carbon atom bearing positive charge *exerts an electron-releasing inductive effect* and thus reduces the positive charge of the carbon atom to which it is attached ; in doing so the alkyl group itself becomes somewhat positive. This dispersal of charge stabilizes the carbocation.



Methyl cation | Primary carbocation | Secondary carbocation | Tertiary carbocation

---

*In a party consisting of the father, mother and a small child, the slowest moving member (the child) determines the speed of the party as a whole. Similarly in a reaction proceeding in steps, the slowest step determines the speed of the overall reaction.

A tertiary carbocation with three alkyl groups is, therefore, more stable than a secondary carbocation with two alkyl groups which in turn is more stable than a primary carbocation with only one alkyl group, the methyl carbocation, with no alkyl groups attached to the electron-deficient carbon, is least stable of all. Thus stability of carbocations is in the following order :

$$3^\circ > 2^\circ > 1^\circ > CH_3^+$$

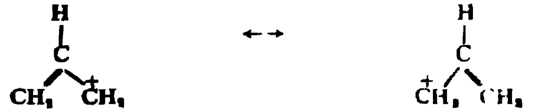
The presence of an electron-withdrawing atom or group tends to intensify the positive charge on the electron-deficient carbon, and hence makes the carbocation less stable.

***The stability of a carbocation** depends chiefly upon the tendency of the attached groups to release or withdraw electrons.*

The more stable the carbocation, the more easily it is formed. While listing carbocations in the order of their ease of formation, we find that this is also the order of their stability as given below :

$$3^\circ > 2^\circ > 1^\circ > CH_3^+$$

Stabilization of a carbocation can also be accomplished by resonance. If the carbon atom which is lacking an electron pair is adjacent to an unsaturated system one can draw resonance structures in which the positive charge has been delocalized over the molecular system. The resonance stabilization leads to a marked increase in the stability of the carbocation in comparison to the simple alkyl cations mentioned above. One typical example of resonance-stabilized carbocations is the allyl cation.



Methods of Formation. Some important methods by which carbocations may be formed, are :

(*a*) *By Heterolysis.*

$$(CH_3)_3C{-}X \longrightarrow \underset{\substack{\textit{tert}\text{-butyl}\\ \text{cation}}}{(CH_3)_3C^+} + X^-$$

(*b*) *By Protonation of alkenes or alcohols.*

$$CH_2{=}CH_2 \overset{H^+}{\rightleftharpoons} \overset{+}{C}H_2{-}CH_3$$

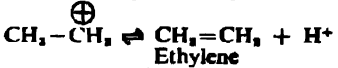
$$R{-}\ddot{O}H \overset{H^+}{\rightleftharpoons} R{-}\overset{+}{O}H_2 \overset{-H_2O}{\rightleftharpoons} R^+$$

(*c*) By decomposition of certain compounds, *e.g.*, diazo compounds.

$$\underset{\substack{\text{Benzene diazo-}\\ \text{nium chloride}}}{C_6H_5{-}N_2{-}Cl} \xrightarrow{-Cl^-} C_6H_5{-}N_2^+ \xrightarrow{-N_2} \underset{\substack{\text{Phenyl}\\ \text{cation}}}{C_6H_5^+}$$

Reactions of Carbocations. A carbocation may undergo any of the following reactions :

(*a*) ***Elimination of a proton to form an alkene.*** **For example,** ***ethyl cation loses a proton to form ethylene.***

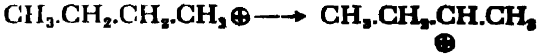


$$\overset{\oplus}{CH_3-CH_2} \rightleftharpoons CH_2=CH_2 + H^+$$

Ethylene
(*an alkene*)

(*b*) *Rearrangement to form a* ***more stable carbocation.*** **For** example,

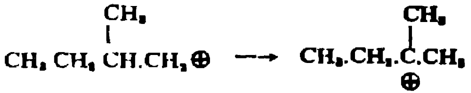
(*i*) Butyl cation rearranges to give more stable **sec-Butyl** cation.



$$CH_3.CH_2.CH_2.CH_2\oplus \longrightarrow CH_3.CH_2.\underset{\oplus}{CH}.CH_3$$

(*Less stable primary*) (***More stable secondary***)

(*ii*) 2-methyl-1-butyl cation **rearranges to 2-methyl-2-butyl** cation.

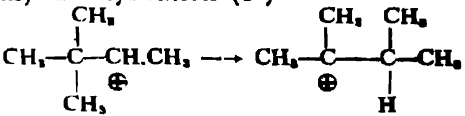


$$CH_3.CH_2.\overset{\overset{\displaystyle CH_3}{|}}{CH}.CH_2\oplus \longrightarrow CH_3.CH_2.\underset{\oplus}{\overset{\overset{\displaystyle CH_3}{|}}{C}}.CH_3$$

(*Less stable primary*) (*More stable tertiary*)

Rearrangement in (*i*) and (*ii*) is caused by the **migration of** hydrogen with a pair of electrons called a **hydride shift.**

(*iii*) 3, 3-dimethyl-1-2-butyl cation (2°) **rearranges to give more** stable 2, 3-dimethyl-2-butyl cation (3°)

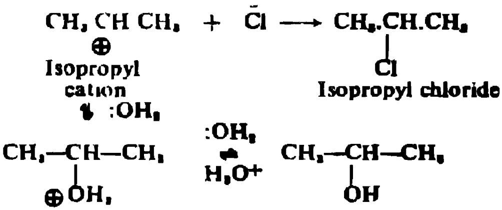


$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-\underset{\oplus}{CH}.CH_3 \longrightarrow CH_3-\underset{\oplus}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3$$

(*Secondary*) (***Tertiary***)

Here rearrangement is caused by the **migration of an alkyl** group called **alkyl shift.**

(*c*) *It may combine with a* ***negative ion or another basic molecule.*** For example,



$$CH_3.\underset{\oplus}{CH}.CH_3 + \overset{-}{Cl} \longrightarrow CH_3.\underset{\underset{\displaystyle Cl}{|}}{CH}.CH_3$$

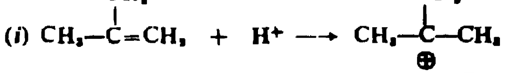
Isopropyl cation Isopropyl chloride

$\downarrow$:OH$_2$

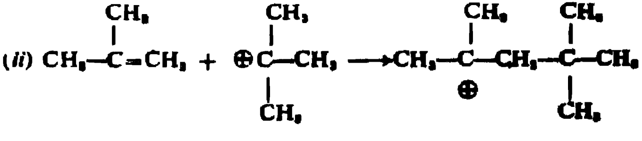
$$CH_3-\underset{\underset{\displaystyle \oplus OH_2}{|}}{CH}-CH_3 \underset{H_3O^+}{\overset{:OH_2}{\rightleftharpoons}} CH_3-\underset{\underset{\displaystyle OH}{|}}{CH}-CH_3$$

Protonated alcohol **Isopropyl alcohol**

(*d*) ***It may add to an alkene to form a larger carbocation.*** **For** example, dimerization of isobutylene is **explained as under :**

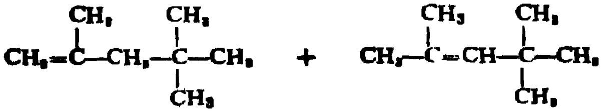


$$(i)\ CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2 + H^+ \longrightarrow CH_3-\underset{\oplus}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3$$



$$(ii)\ CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2 + \oplus\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3 \longrightarrow CH_3-\underset{\oplus}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3$$

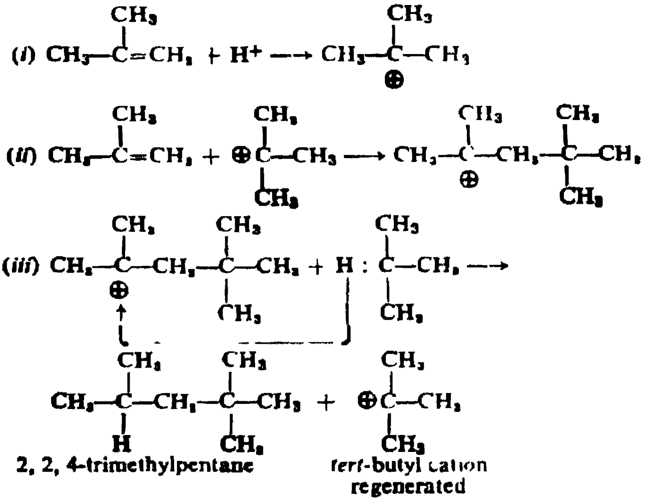
(*iii*) In the 3rd step the resultant larger carbocation loses a proton in two possible ways to yield a mixture of the following two alkenes :



$$CH_2{=}\overset{\overset{\textstyle CH_3}{|}}{C}{-}CH_2{-}\underset{\underset{\textstyle CH_3}{|}}{\overset{\overset{\textstyle CH_3}{|}}{C}}{-}CH_3 \quad + \quad CH_3{-}\overset{\overset{\textstyle CH_3}{|}}{C}{=}CH{-}\underset{\underset{\textstyle CH_3}{|}}{\overset{\overset{\textstyle CH_3}{|}}{C}}{-}CH_3$$

(*e*) *It might abstract a hydride ion to form an alkane.* Isobutylene and isobutane react in the presence of an acid catalyst to form 2, 2, 4-trimethylpentane or iso-octane.

This is addition of an alkane to an alkene (**alkylation**). This is explained as follows :



$$(i)\quad CH_3{-}\overset{\overset{\textstyle CH_3}{|}}{C}{=}CH_2 + H^+ \longrightarrow CH_3{-}\underset{\oplus}{\overset{\overset{\textstyle CH_3}{|}}{C}}{-}CH_3$$

$$(ii)\quad CH_3{-}\overset{\overset{\textstyle CH_3}{|}}{C}{=}CH_2 + \oplus\underset{\underset{\textstyle CH_3}{|}}{\overset{\overset{\textstyle CH_3}{|}}{C}}{-}CH_3 \longrightarrow CH_3{-}\underset{\oplus}{\overset{\overset{\textstyle CH_3}{|}}{C}}{-}CH_2{-}\underset{\underset{\textstyle CH_3}{|}}{\overset{\overset{\textstyle CH_3}{|}}{C}}{-}CH_3$$

$$(iii)\quad CH_3{-}\underset{\oplus}{\overset{\overset{\textstyle CH_3}{|}}{C}}{-}CH_2{-}\underset{\underset{\textstyle CH_3}{|}}{\overset{\overset{\textstyle CH_3}{|}}{C}}{-}CH_3 + H:\underset{\underset{\textstyle CH_3}{|}}{\overset{\overset{\textstyle CH_3}{|}}{C}}{-}CH_3 \longrightarrow$$

$$CH_3{-}\underset{\underset{\textstyle H}{|}}{\overset{\overset{\textstyle CH_3}{|}}{C}}{-}CH_2{-}\underset{\underset{\textstyle CH_3}{|}}{\overset{\overset{\textstyle CH_3}{|}}{C}}{-}CH_3 + \oplus\underset{\underset{\textstyle CH_3}{|}}{\overset{\overset{\textstyle CH_3}{|}}{C}}{-}CH_3$$

2, 2, 4-trimethylpentane

tert-butyl cation regenerated

Steps (*ii*) and (*iii*) are then repeated.

In the step (*iii*) above, the carbocation abstracts a hydride ion from an alkane.

Every carbocation has a carbon atom that is short of two electrons and is, therefore, a Lewis acid. For this reason every carbocation can react with a substance which can supply an electron pair (a Lewis base).

All these reactions of the carbocation *provide a pair of electrons to complete the octet of the positively charged carbon.*

7. **Ionic Mechanism.**—Ionic mechanisms for a few individual reactions are given below :

(1) **Substitution Reactions.** Polar substitution reactions can be of two types :

(*a*) **Nucleophilic Substitution Reactions.** These are reactions in which the attacking reagent is a nucleophile. Some examples of such reactions are :

(i) Hydrolysis of Alkyl Halides (*A Substitution Reaction*).

Alkyl halides are hydrolysed to *alcohols* very slowly by water but rapidly by boiling with aqueous alkalis or with silver oxide suspended in boiling water.

$$R|X + K|OH \longrightarrow \underset{\text{Alcohol}}{ROH} + KX$$
$$(\text{Aqueous})$$

The hydrolysis is an example of nucleophilic substitution (S_N) because the attacking reagent is a nucleophilic one. This type of heterolytic reaction in solution can be explained in terms of two different mechanisms (unimolecular or bimolecular) as follows :

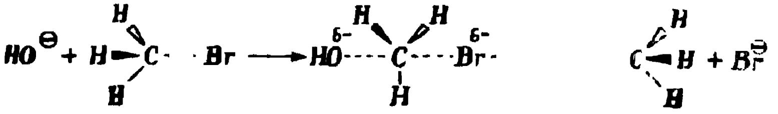
Unimolecular Mechanism. In this it is assumed that the reaction is completed in two stages. In the first stage *slow* heterolysis occurs yielding a carbocation. In the second stage a *rapid* combination occurs between the carbocation and the substituting nucleophilic reagent. Since the first step involving only one molecule is the rate-determining step, the mechanism is termed *unimolecular* and labelled as S_N1. This may be represented as follows :

$$\underset{\text{Alkyl halide}}{R—X} \xrightarrow[\text{1st stage}]{\text{slow}} \overset{\delta+\ \ \delta-}{R\ldots X} \xrightarrow{\text{fast}} X^- + R^+ \xrightarrow[\text{fast, 2nd stage}]{OH^-} \underset{\text{Alcohol}}{ROH}$$

Bimolecular Mechanism. According to this, hydrolysis is assumed to be a *one-stage process* wherein two molecules simultaneously undergo covalency change. The rate-determining step is the formation of the intermediate transition state. This mechanism is, therefore, termed bimolecular and labelled as S_N2 standing for Substitution Nucleophilic Bimolecular.

This type of reaction is accompanied by Walden inversion and may be represented as follows :

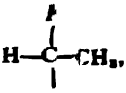
When OH⁻ collides with a CH_3Br molecule at the face farthest from Br and if the energy of collision is sufficient, a C—OH bond is formed and the C—Br bond breaks. In the transition state the carbon atom may be pictured to be partially bonded to both —OH and —Br (the C—Br bond has stretched but not completely broken and the C—OH bond is not completely formed). In this transition state the —OH and —Br are as far apart as possible, the three H and the C are in the same plane (sp^2 hybridization) the bond angles being 120°. The C—H bonds are thus arranged (in the transition complex stage) like the spokes of a wheel while —OH and —Br are lying *along the axle* on opposite sides. When the —Br completely leaves, —OH has taken a position opposite to that previously occupied by the —Br. The alcohol formed has opposite configuration to that of the bromide (or has been inverted just as an umbrella turns inside out in a high wind). The reaction is said to proceed with *inversion of configuration.*



(nucleophile approaches)

transition complex (OH has a diminished negative charge as it begins to share its electrons with C, Br has developed a partial negative charge as it has partly removed a pair of electrons from C)

configuration inverted as Br⁻ leaves.

As H atoms of $—CH_3$ are replaced by bulkier groups (*e.g.*,  $H—\overset{|}{\underset{|}{C}}—CH_3$, $—\overset{\overset{CH_3}{|}}{\underset{|}{C}}—CH_3$, etc.) there is increased crowding around the carbon atom and therefore, the approach of the attacking nucleophile is hindered (*Steric hindrance*) and the reaction slows down The presence of bulkier groups makes the transition complex less stable due to overcrowding. It is, therefore, not readily formed. In general for an S_N2 reaction the order of activity of alkyl halides is :

$$CH_3X > \text{primary halides} > \text{secondary} > \text{tertiary}$$

It has been found that tertiary alkyl halides usually react by unimolecular mechanism whereas the primary alkyl halides usually react by bimolecular mechanism.

(*ii*) **Formation of alkyl halides.**

$$ROH + HBr \rightarrow RBr + H_2O$$

$$R\underset{\cdot\cdot}{O}H + H^{+} \rightarrow R\overset{\oplus}{\underset{\underset{H}{\cdot\cdot}}{O}}H$$

$$\overset{\ominus}{Br} + R\overset{\oplus}{\underset{\underset{H}{\cdot\cdot}}{O}}H \rightarrow Br—R + H_2O$$

(*iii*) **Cleavage of ethers.**

$$R—O—R' + HI \rightarrow ROH + R'I$$

$$R—\underset{\cdot\cdot}{O}—R' + H^{+} \rightarrow R—\overset{\oplus}{\underset{\underset{H}{\cdot\cdot}}{O}}—R'$$

$$I^- + R—\overset{\oplus}{\underset{\underset{H}{\cdot\cdot}}{O}}—R' \rightarrow I—R + R'OH$$

(*iv*) **Formation of ethers** (*Williamson's synthesis*).

$$RI + NaOR' \rightarrow R—O—R' + NaI$$

$$R'O^- + R—I \rightarrow R'—O—R + I^-$$

(*b*) **Electrophilic Substitution Reactions.** These are reactions in which the attacking reagent is an electrophile. Such reactions are very common in aromatic compounds—*see Chapter 23.*

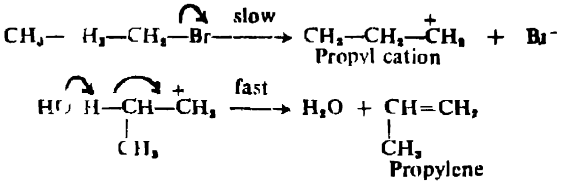
(2) **Elimination Reactions.** Some examples of elimination reactions are :

(*i*) **Removal of halogen acid from an alkyl halide.** When an alkyl halide is boiled with alcoholic potash, an olefin is obtained, *e.g.*, propyl bromide gives propylene.

$$\underset{\text{Propyl bromide}}{CH_3.CH_2.CH_2.Br} + \underset{(alcoholic)}{KOH} \longrightarrow \underset{\text{Propylene}}{CH_3.CH{=}CH_2} + KBr + H_2O$$

According to Hughes and Ingold (1941), the **elimination reaction** between an alkyl halide and aqueous potash may proceed by either a unimolecular (E1) or a bimolecular (E2) mechanism.

(*i*) E1 *mechanism* :



$$CH_3-CH_2-CH_2-Br \xrightarrow{slow} CH_3-CH_2-\overset{+}{C}H_2 + Br^-$$

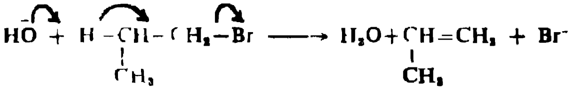
Propyl cation

$$HO^- \; H-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\overset{+}{C}H_2 \xrightarrow{fast} H_2O + \underset{\displaystyle CH_3}{\underset{|}{CH}}=CH_2$$

Propylene

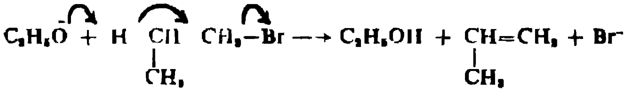
Here again it is assumed that the reaction is completed in two stages. In the first stage slow heterolysis occurs yielding a carbocation. In the second stage HO^- ion removes a proton from the carbocation and this elimination is rapid. The first stage involves only one molecule and being slow determines the order of the reaction which is, therefore, unimolecular elimination (E1) reaction.

(*ii*) E2 *mechanism* :



$$\overset{-}{HO} + H-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-Br \longrightarrow H_2O + \underset{\displaystyle CH_3}{\underset{|}{CH}}=CH_2 + Br^-$$

On the other hand, with alcoholic potash which contains potassium ethoxide $C_2H_5\overset{-}{O}\overset{+}{K}$, the reaction tends to take place by **E2** mechanism as follows :



$$C_2H_5\overset{-}{O} + H \; \underset{\displaystyle CH_3}{\underset{|}{CH}} \; CH_2-Br \longrightarrow C_2H_5OH + \underset{\displaystyle CH_3}{\underset{|}{CH}}=CH_2 + Br^-$$

In an alkyl halide the carbon atom carrying the halogen becomes more and more branched as we proceed from 1° to 2° to 3°. This increased branching has two results :

(*i*) It provides greater number of hydrogens for attack by base and hence a more favourable probability factor towards elimination ; and

(*ii*) It leads to more highly branched, *i.e.*, more stable transition state and lower E_{act}.

As a result of these two factors **in dehydrohalogenation the order of reactivity of RX is 3°>2°>1°.**

(*ii*) **Dehydration of Alcohols.** The generally accepted mechanism for the dehydration of alcohols is summarized in the following steps

(*i*) *The alcohol unites with a* H^+ *to form the* ***protonated alcohol.***

$$CH_3CH_2-\ddot{O}H \xrightleftharpoons{H^+} CH_3.CH_2-\overset{\oplus}{\ddot{O}}H_2$$

Alcohol Protonated alcohol

(*ii*) *The protonated alcohol dissociates into water and a carbocation*

$$CH_3CH_2-\overset{\oplus}{\underset{\cdot\cdot}{O}}H_2 \rightleftharpoons \underset{\text{Carbocation}}{CH_3-\overset{\oplus}{C}H_2} + H_2O$$

(*iii*) *The carbocation loses a proton to form the alkene.*

$$CH_3-\overset{\oplus}{C}H_2 \rightleftharpoons \underset{\substack{\text{Ethylene}\\ (\textit{an alkene})}}{CH_2=CH_2} + H^+$$

In some cases the carbocation may undergo rearrangement to give a more stable carbocation before losing a proton. For example, dehydration of 1-butanol gives 2-butene. This can be explained as follows :

$$\underset{\text{1-Butanol}}{CH_3.CH_2.CH_2.CH_2.OH} \xrightarrow{H^+} \underset{\text{Protonated alcohol}}{CH_3.CH_2CH_2CH_2\overset{+}{O}H_2}$$

$$\xrightarrow{-H_2O} \underset{\text{1-Butyl cation}}{CH_3CH_2.CH_2.CH_2\,\oplus} \xrightarrow[\text{ment}]{\text{Rearrange-}} \underset{\text{2-Butyl cation}}{CH_3.CH_2.\underset{\oplus}{C}H.CH_3}$$

$$\xrightarrow{-H^+} \underset{\text{2-Butene}}{CH_3.CH=CH.CH_3}$$

It is chiefly because of the greater certainty as to where the double bond will appear that dehydrohalogenation is often preferred over dehydration as a method of preparation of alkenes.

The carbocation is formed by dissociation of protonated alcohol involving separation of charged particle R⊕ from the neutral molecule H_2O. This obviously requires much less energy than formation of R⊕ from alcohol itself which involves separation of a positive particle (R⊕) from a negative particle (OH^-).

$\overset{\oplus}{ROH_2} \rightarrow R^{\oplus} + H_2O$ Weak base : *good leaving agent* **Easy**

$ROH \rightarrow R^{\oplus} + OH^-$ Strong base : *poor leaving agent* **Difficult**

Viewed in another way, the carbocation is a Lewis acid. It can release a weak base (H_2O) much more readily than it can release a strong base (OH^-).

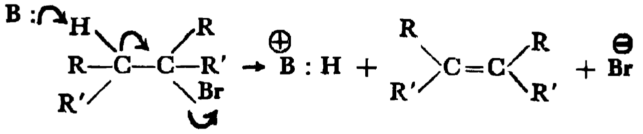
Dehydration of alcohol, therefore, requires the presence of an acid (to give protonated alcohol) and the application of heat. This is carried out either by heating it with sulphuric acid or phosphoric acid or by passing alcohol vapours over heated alumina (serving as Lewis acid) at 525K.

Ease of dehydration of alcohol is : 3° > 2° > 1°

This being the order of stability and the ease of formation of carbocations from them.

Stereospecificity in E2 Elimination. A high degree of **stereospecificity is exhibited by E2 elimination reactions. These**

proceed more readily if the atoms or groups to be eliminated are located trans to each other.



The base B: abstracts a proton and the electron pair so released attacks the α-carbon atom probably from the back* followed by the displacement of the leaving group, Br. The H atom being eliminated, the leaving group Br and the two carbon atoms Cα and Cβ should all be coplanar in the transition state.

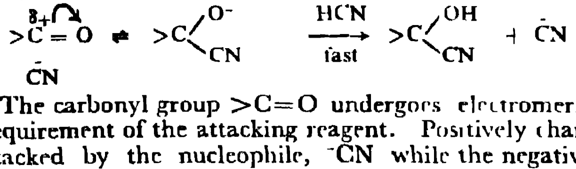
(3) **Addition Reactions**. The positive end of a polar molecule, being electron deficient, is termed electrophile and its negative end is electron-rich or nucleophile.

An addition reaction in which the first step is slow addition (rate-determining step) of a nucleophile is termed *Nucleophilic addition reaction.* Following this rate-determining step, the intermediate then yields the final product by abstracting a proton from some source, usually the solvent.

Similarly, when the first step is the slow addition of an electrophile (rate-determining step) resulting in the formation of a carbocation, it is called *Electrophilic addition reaction.* Following this rate-determining step, the carbocation combines rapidly with some nucleophile, $Nu^{\ominus}$ like the second step in S_N1 reaction. Some examples of addition reactions are :

(*i*) **Nucleophilic Addition of hydrogen cyanide to a carbonyl group**. Liquid HCN gives an addition compound (a cyanohydrin) with aldehydes and ketones (both containing a carbonyl group, $>C=O$). It is found that the addition is catalysed by bases and retarded by acids. From this it is concluded that the addendum was the cyanide ion, ^-CN and not HCN directly.

The mechanism suggested for the base-catalysed formation of cyanohydrins in liquid HCN is as follows :



The carbonyl group $>C=O$ undergoes electromeric effect at the requirement of the attacking reagent. Positively charged carbon is attacked by the nucleophile, ^-CN while the negatively charged oxygen atom is attacked by the electrophile, H^+. Positively charged carbon, being a less stable arrangement, is attacked first and the negatively charged oxygen, being more stable arrangement, is attacked later.

(*ii*) **Electrophilic Addition of halogens to olefins**. Ethylene gives an addition product with bromine.

$$\underset{\text{Ethylene}}{CH_2=CH_2}+Br_2 \longrightarrow \underset{\text{Ethylene bromide}}{CH_2Br—CH_2Br}$$

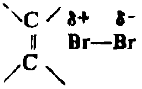
---

*In S_N2 reactions also the attacking group approaches the molecule from the back *i.e.*, from the side away from the leaving group.

Electronic Mechanism. The high reactivity of the olefinic bond is due to the presence of two π-electrons which readily undergo electromeric effect at the requirement of the attacking reagent. During addition of bromine, ethylene undergoes electromeric effect.

$$\overset{\curvearrowright}{CH_2=CH_2} \longrightarrow \overset{+}{C}H_2-\overset{\bar{..}}{C}H_2$$

A halogen molecule is non-polar. In the vicinity of a dense electron cloud of the carbon-carbon double bond, however, it gets polarised



Polarization of Br_2 by a double bond

The polarized bromine molecule approaches the ethylene molecule forming the transition complex which then breaks as given below :

$$\overset{\delta-}{Br}-\overset{\delta+}{Br}\ \ldots\overset{-}{C}H_2-\overset{+}{C}H_2 \longrightarrow \overset{-}{Br}: + Br-CH_2-\overset{+}{C}H_2$$

Transition complex

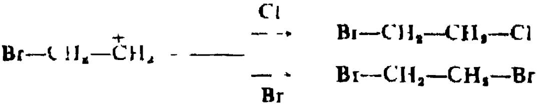
Next, the bromide ion (Br^-) attaches to the positively charged carbon atom.

$$Br-CH_2-\overset{+}{C}H_2 + \overset{-}{Br} \longrightarrow \underset{\text{Ethylene bromide}}{Br-CH_2-CH_2-Br}$$

Combining these equations, we can represent the addition as :

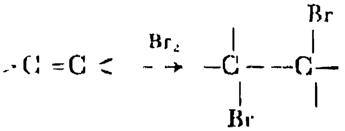
$$\underset{\text{Bromine}}{\overset{\curvearrowright}{Br-Br}}\ \underset{\text{Ethylene}}{\overset{\curvearrowleft}{CH_2=CH_2}} \longrightarrow BrCH_2.\overset{+}{C}H_2 + \overset{\curvearrowleft}{Br^-} \rightarrow \underset{\text{Ethylene bromide}}{BrCH_2.CH_2Br}$$

That out of the two bromine atoms Br^+ adds first and the addition of Br^- takes place next is supported by the formation of a mixture of CH_2Br-CH_2Cl and CH_2Br-CH_2Br when ethylene is treated with bromine water containing sodium chloride. This is because both Br^- and Cl^- ions are available in the second step and both of them compete for the positively charged carbon atom in $Br-CH_2-\overset{+}{C}H_2$.



$$Br-CH_2-\overset{+}{C}H_2 \begin{cases} \xrightarrow{Cl} Br-CH_2-CH_2-Cl \\ \xrightarrow[Br]{} Br-CH_2-CH_2-Br \end{cases}$$

Such additions have been found to be stereochemically trans.

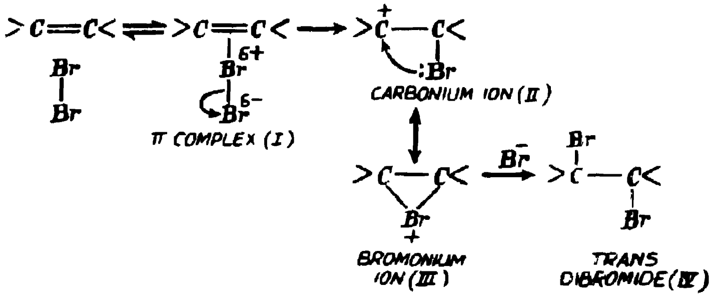


$$>C=C< \xrightarrow{Br_2} -\underset{\substack{| \\ Br}}{C}-\overset{\substack{Br \\ |}}{C}-$$

Trans addition of bromine to an olefin is supposed to proceed through the following steps :

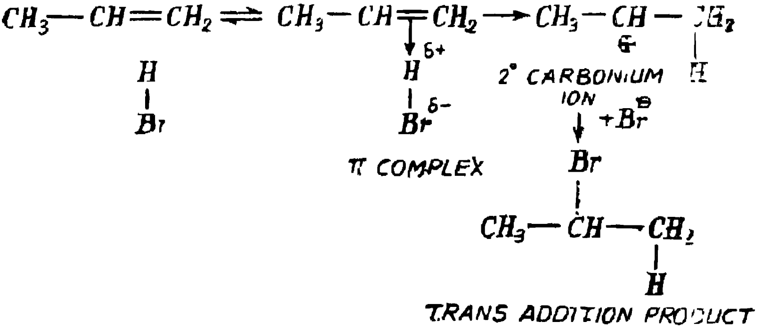
(*i*) Bromine interacts with the π electrons to form a π complex (I) which then leads to the formation of a σ bond in the carbocation (II) or the bromonium ion (III).

(*ii*) Carbocation or the bromonium ion is finally attacked by the nucleophile Br^- resulting in the formation of dibromide (IV).



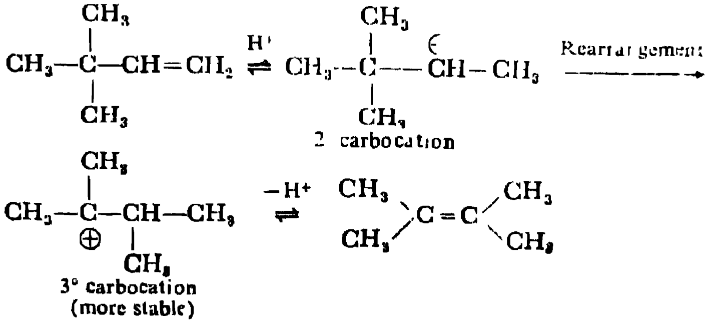
(*iii*) **Electrophilic Addition of Halogen acids to Olefins.** In this reaction the first step (which is also the rate-determining step) is the addition of H^+ to form a π complex which subsequently leads to the formation of a carbocation. The second step is the attack of the nucleophile X^- to form a trans addition product.

During the addition of HBr to propylene the two steps are : (*i*) addition of H^+ to form more stable isopropyl $\underset{\oplus}{\text{c}}$ation (not primary) and finally (*ii*) addition of Br to yield a trans product, isopropyl bromide.



(4) **Rearrangement.** We are already familiar with the fact that a carbocation rearranges itself to give a more stable carbocation. Examples of some reactions involving rearrangement are

(*i*) **Rearrangement of Alkenes.** This takes place in the presence of acids.



(*ii*) **Rearrangement of Alkyl halides.** 1-Bromobutane on heating to 575K or at lower temperature in presence of $AlCl_3$ undergoes rearrangement to give 2-Bromobutane as follows :

$$\underset{\text{1-Bromobutane}}{CH_3CH_2CH_2CH_2Br} \xrightarrow{-Br^-} \underset{1^\circ\text{ carbocation}}{CH_3CH_2CH_2\overset{+}{C}H_2} \xrightarrow[\text{Hydride shift}]{\text{Rearrangement}}$$

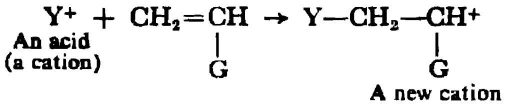
$$\underset{\substack{\text{More stable}\\ 2^\circ\text{ carbocation}}}{CH_3CH_2\overset{+}{C}HCH_3} \xrightarrow{Br^-} \underset{\text{2-Bromobutane}}{CH_3CH_2CHBrCH_3}$$

(5) **Polymerisation.** Some examples of polymerisation are :

(1) **Polymerisation of substituted ethylenes, $CH_2{=}CHG$.**

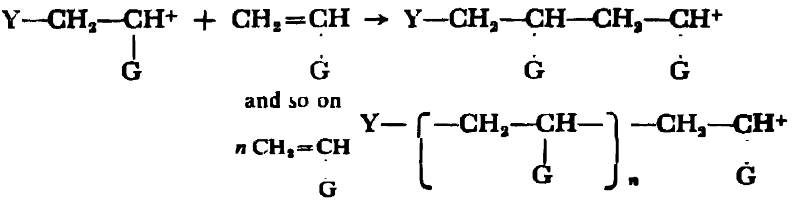
(*a*) **Cationic mechanism.**

(*i*) *Initiation step* :



$$\underset{\substack{\text{An acid}\\ \text{(a cation)}}}{Y^+} + CH_2{=}\underset{\substack{|\\ G}}{CH} \rightarrow \underset{\text{A new cation}}{Y{-}CH_2{-}\underset{\substack{|\\ G}}{CH^+}}$$

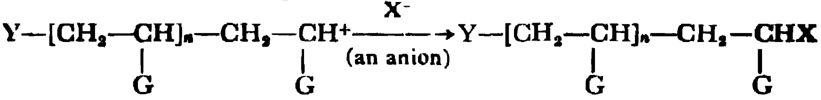
(*ii*) *Propagation steps* :



$$Y{-}CH_2{-}\underset{\substack{|\\ G}}{CH^+} + CH_2{=}\underset{\substack{|\\ G}}{CH} \rightarrow Y{-}CH_2{-}\underset{\substack{|\\ G}}{CH}{-}CH_2{-}\underset{\substack{|\\ G}}{CH^+}$$

$$\xrightarrow[n\,CH_2=\underset{\substack{|\\ G}}{CH}]{\text{and so on}} Y{-}\left[{-}CH_2{-}\underset{\substack{|\\ G}}{CH}{-}\right]_n{-}CH_2{-}\underset{\substack{|\\ G}}{CH^+}$$

(*iii*) *Termination step* :

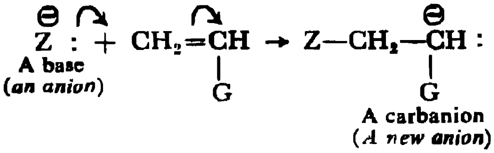


$$Y{-}[CH_2{-}\underset{\substack{|\\ G}}{CH}]_n{-}CH_2{-}\underset{\substack{|\\ G}}{CH^+} \xrightarrow[\text{(an anion)}]{X^-} Y{-}[CH_2{-}\underset{\substack{|\\ G}}{CH}]_n{-}CH_2{-}\underset{\substack{|\\ G}}{CHX}$$

Polymer

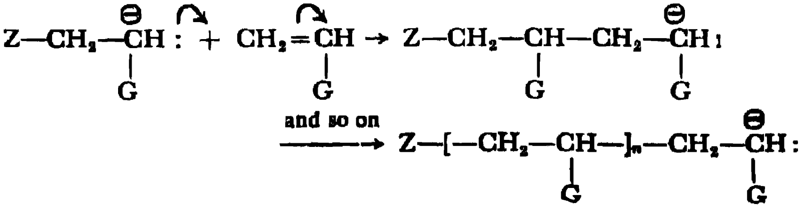
(*b*) **Anionic mechanism**

(*i*) *Initiation step* :



$$\underset{\substack{\text{A base}\\ \text{(an anion)}}}{\overset{\ominus}{Z}\,:} + CH_2{=}\underset{\substack{|\\ G}}{CH} \rightarrow \underset{\substack{\text{A carbanion}\\ \text{(A new anion)}}}{Z{-}CH_2{-}\underset{\substack{|\\ G}}{\overset{\ominus}{CH}}\,:}$$

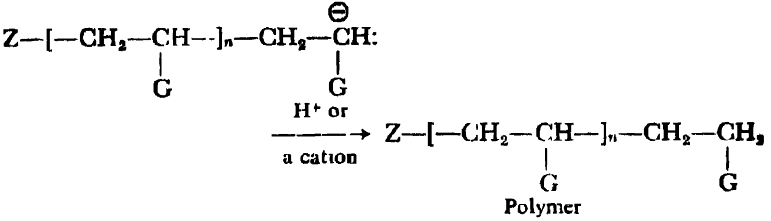
(*ii*) *Propagation steps* :



$$Z{-}CH_2{-}\underset{\substack{|\\ G}}{\overset{\ominus}{CH}}\,: + CH_2{=}\underset{\substack{|\\ G}}{CH} \rightarrow Z{-}CH_2{-}\underset{\substack{|\\ G}}{CH}{-}CH_2{-}\underset{\substack{|\\ G}}{\overset{\ominus}{CH}}\,:$$

$$\xrightarrow{\text{and so on}} Z{-}[{-}CH_2{-}\underset{\substack{|\\ G}}{CH}{-}]_n{-}CH_2{-}\underset{\substack{|\\ G}}{\overset{\ominus}{CH}}\,:$$

(*iii*) *Termination step* :



$$Z-[-CH_2-\underset{\displaystyle G}{\underset{|}{C}H}-]_n-CH_2-\underset{\displaystyle G}{\underset{|}{\overset{\ominus}{C}H}}: \xrightarrow[\text{a cation}]{H^+ \text{ or}} \underset{\text{Polymer}}{Z-[-CH_2-\underset{\displaystyle G}{\underset{|}{C}H}-]_n-CH_2-\underset{\displaystyle G}{\underset{|}{C}H_3}}$$

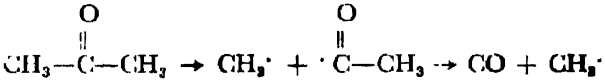
(2) **Polymerisation of Isobutylene.** *See page 1·148.*

8. Free Radicals. As stated earlier *free radicals are species with one* (*or more*) *unpaired electron*(*s*) obtained by the homolytic fission of a covalent bond.

Methods of formation. Some important methods by which radicals may be formed are :

(*a*) **Photochemical fission.** Absorption of electro-magnetic radiation by a molecule causes bond fission. For example chlorine, bromine, acetone, peroxides, etc., are susceptible to photochemical fission.

$$Cl-Cl \rightarrow Cl^{\cdot} + Cl^{\cdot}$$



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \rightarrow CH_3^{\cdot} + {}^{\cdot}\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \rightarrow CO + CH_3^{\cdot}$$

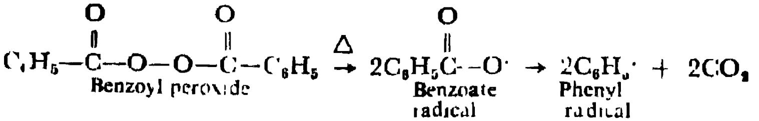
(*b*) **Thermal fission.** Pyrolysis of all organic compounds yields radicals, *e.g.*, (*i*) Lead tetraethyl on heating decomposes to give $C_2H_5^{\cdot}$ free radicals.

$$Pb(C_2H_5)_4 \rightarrow Pb + 4C_2H_5^{\cdot}$$

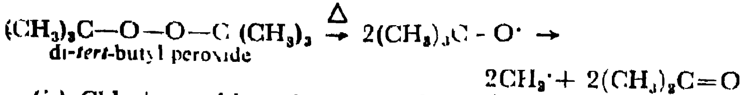
(*ii*) Azomethane decomposes at 575K, by homolytic fission of C—N bond resulting in the formation of extremely stable nitrogen molecule.

$$CH_3-N=N-CH_3 \rightarrow 2CH_3^{\cdot} + N\equiv N$$

(*iii*) Organic peroxides are easily decomposed at quite low temperatures (ranging between room temperature and 375K) due to the presence of the very weak O—O bond (bond dissociation energy ≈125 kJ mol^{-1}). For example, dibenzoyl peroxide and di-*tert*-butyl peroxide.



$$\underset{\text{Benzoyl peroxide}}{C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-O-O-\overset{\overset{\displaystyle O}{\|}}{C}-C_6H_5} \xrightarrow{\Delta} \underset{\text{Benzoate radical}}{2C_6H_5\overset{\overset{\displaystyle O}{\|}}{C}-O^{\cdot}} \rightarrow \underset{\text{Phenyl radical}}{2C_6H_5^{\cdot}} + 2CO_2$$



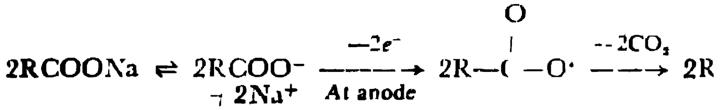
$$\underset{\text{di-}tert\text{-butyl peroxide}}{(CH_3)_3C-O-O-C(CH_3)_3} \xrightarrow{\Delta} 2(CH_3)_3C-O^{\cdot} \rightarrow 2CH_3^{\cdot} + 2(CH_3)_2C=O$$

(*iv*) Chlorine and bromine also undergo thermal fission to yield free radicals.

(*c*) **Oxidation/Reduction reactions.** These include oxidation/reduction reactions by inorganic ions, metals or electrolysis resulting in single electron transfers. For example, (*i*) Use of ferrous ion to catalyse oxidation with hydrogen peroxide in Fenton's reagent.

$$H_2O_2 + Fe^{2+} \rightarrow HO^{\cdot} + OH^- + Fe^{3+}$$

(*ii*) Electrolysis of an aqueous solution of the alkali salt of a fatty acid (Kolbe's electrolytic synthesis of hydrocarbons).



$$2RCOONa \rightleftharpoons \underset{+\ 2Na^+}{2RCOO^-} \xrightarrow[\text{At anode}]{-2e^-} 2R\text{—}\overset{\overset{\displaystyle O}{|}}{C}\text{—}O^{\cdot} \xrightarrow{-2CO_2} 2R$$

Reactions of Free Radicals. Radicals undergo the following types of reactions :

(*a*) **Combination.** Free radicals may undergo dimerisation. Two different radicals combine on colliding with each other. For example :

$$Cl^{\cdot} + Cl^{\cdot} \rightarrow Cl_2$$
$$CH_3^{\cdot} + CH_3^{\cdot} \rightarrow CH_3\text{—}CH_3$$
$$CH_3^{\cdot} + Cl^{\cdot} \rightarrow CH_3\text{—}Cl$$

(*b*) **Disproportionation.** This involves transfer of hydrogen between two radicals. This is energetically more favourable since it involves fission of one bond and formation of the new bonds

$$\underset{\text{Two ethyl radicals}}{2CH_3CH_2^{\cdot}} \rightarrow \underset{\text{Ethane}}{CH_3CH_3} + \underset{\text{Ethylene}}{CH_2{=}CH_2}$$

(*c*) **Abstraction.** Free radicals may abstract an atom (usually a hydrogen atom) from a saturated organic compound. For example

$$\underset{\text{Methyl radical}}{CH_3^{\cdot}} + \underset{\text{Ethane (A saturated compound)}}{H\text{—}C_2H_5} \rightarrow \underset{\text{Methane}}{CH_4} + \underset{\text{Ethyl radical}}{C_2H_5^{\cdot}}$$

$$Cl^{\cdot} + H\text{—}CH_3 \rightarrow HCl + {}^{\cdot}CH_3$$

In general, the reaction

$$X^{\cdot} + H\text{—}R \rightarrow XH + R^{\cdot}$$

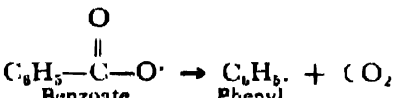
will proceed if the energy of the X—H bond is greater than the energy of the H—R bond because in that case products are more stable than the starting materials.

(*d*) **Addition to Multiple Bonds.**

$$\underset{\text{Propylene}}{CH_3\text{—}CH{=}CH_2} + \underset{\text{radical}}{Br^{\cdot}} \rightarrow \underset{\text{Another radical}}{CH_3\text{—}\dot{C}H\text{—}CH_2Br}$$

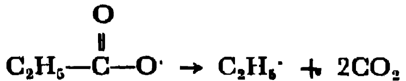
(*e*) **Fragmentation.** Certain radicals undergo fission resulting in the formation of a new radical and a non-radical fragment *e.g.*,

(*i*)



$$\underset{\text{Benzoate Radical}}{C_6H_5\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}O^{\cdot}} \rightarrow \underset{\text{Phenyl radical}}{C_6H_5^{\cdot}} + CO_2$$

(ii)



$$C_2H_5—\overset{\overset{O}{\|}}{C}—O^{\cdot} \rightarrow C_2H_5^{\cdot} + 2CO_2$$

Propionate radical → Ethyl radical

Stability of Free Radicals. When an alkane dissociates into free radicals (R—H→ R˙ + H˙) energy equal to its bond dissociation energy has to be supplied to it increasing the P.E. of the free radical.

Smaller the bond dissociation energy, greater the ease with which it is formed and less will be its P.E. making it more stable.

Bond dissociation energies of some radicals are given below

$CH_3—H \longrightarrow CH_3^{\cdot} + H^{\cdot}$; $\Delta H = 435{\cdot}1$ kJ

Methane → Methyl radical

$CH_3—CH_2—H \longrightarrow CH_3—CH_2^{\cdot} + H^{\cdot}$; $\Delta H = 411$ kJ

Ethane → Ethyl radical (a 1° radical)

$(CH_3)_2CH—H \longrightarrow (CH_3)_2CH^{\cdot} + H^{\cdot}$; $\Delta H = 395{\cdot}4$ kJ

Propane → Isopropyl radical (a 2° radical)

$(CH_3)_3C-H \longrightarrow (CH_3)_3C^{\cdot} + H^{\cdot}$; $\Delta H = 380{\cdot}7$ kJ

Isobutane → *tert*-Butyl radical (a 3° radical)

Dissociation energy decreases and hence P.E. decreases as we pass from $CH_3^{\cdot}$ to $(CH_3)_3C^{\cdot}$ radical. With decrease in P.E., the stability of the radical increases. Hence stability of the radical increases from $CH_3^{\cdot}$ to $(CH_3)_3C^{\cdot}$

Thus we see that their relative stabilities are in the **order** :

$(CH_3)_3\,C^{\cdot} > (CH_3)_2\,CH^{\cdot} > CH_3CH_2^{\cdot} > CH_3^{\cdot}$

tert-Butyl Isopropyl Ethyl Methyl

In general, **stability of free radicals** is in the following order :

3° radical > 2° radical > 1° radical > $CH_3^{\cdot}$

As stated above, smaller the bond dissociation energy, greater the ease with which it is formed. From the values given above it is found that bond dissociation energy increases from $(CH_3)_3C$. to $CH_3^{\cdot}$ radical. $(CH_3)_3C^{\cdot}$ with lowest dissociation energy is most easily formed. In general, **the ease of formation** of a free radical has been found to follow the order :

$$3° > 2° > 1° > CH_3^{\cdot}$$

Relative to alkane from which it is formed, this is also the *order of stability of free radicals*.

Thus, we find that **more stable the free radical, more easily it is formed**.

9. Free Radical Mechanism.—As a result of homolytic fission a molecule breaks into two electrically neutral fragments (atoms or radicals) called *free radicals*. Due to the presence of unpaired electrons in them, the free radicals are highly reactive and have only a transitory existence. They give rise to chain reactions and two such free radicals unite on collision to form a molecule. A few organic reactions explained in terms of free radical mechanism are given on the following pages :

SUBSTITUTION REACTIONS

(1) **Halogenation of Alkanes.** Chlorine or bromine reacts with an alkane on heating or in presence of light, replacing a hydrogen atom by the halogen atom. For example, chlorination of methane gives methyl chloride.

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$

Mechanism of Halogenation. The following series of reactions is postulated to represent the formation of methyl chloride ·

Light dissociates a chlorine molecule into atoms [step (1)] which collide against the methane molecules producing methyl radicals and hydrogen chloride [step (2)]. Methyl radicals in their turn then collide with chlorine molecules to produce methyl chloride and more halogen atoms [step (3)]. This is followed by repetitions of the steps (2) and (3).

$$Cl_2 \xrightarrow{\text{Light}} \underset{\text{Free chlorine atoms}}{Cl^{\cdot} + Cl^{\cdot}} \qquad ..(1)$$

$$CH_4 + Cl^{\cdot} \rightarrow \underset{\substack{\text{Methyl radical} \\ (\textit{extremely reactive})}}{CH_3^{\cdot}} + HCl \qquad .(2)$$

$$CH_3^{\cdot} + Cl_2 \rightarrow CH_3Cl + Cl^{\cdot} \qquad ...(3)$$

Reaction (1) is known as the *initiation step*, while the reactions (2) and (3) are termed the *propagation steps*. This type of reaction is called **a chain reaction**. Many reactions occurring through the agency of free radicals follow a chain reaction mechanism.

The chain reaction does not, however, continue indefinitely. Several other reactions which can occur in the system and are responsible for the stopping of the chains are :

$$Cl^{\cdot} + CH_3^{\cdot} \rightarrow CH_3Cl$$

$$Cl^{\cdot} + Cl^{\cdot} \rightarrow Cl_2$$

$$CH_3^{\cdot} + CH_3^{\cdot} \rightarrow C_2H_6$$

These are termed *chain termination steps*. There are, however, fewer chain termination steps and a very large number of chain propagation steps.

Orientation of Halogenation. The rate of abstraction of hydrogen atom from the alkane to yield free radical has been found to follow the sequence

tertiary (or 3°) > secondary (or 2°) > primary (or 1°).

At room temperature the relative rates of substitution by chlorine per hydrogen atom are

5·0 : 3·8 : 1·0

Using these values we can predict quite well the ratio of the isomeric alkyl chlorides obtained on chlorination of an alkane. For example, during chlorination of *n*-butane

$$\underset{}{CH_3.CH_2.CH_2.CH_3} \xrightarrow[570K]{Cl_2} \underset{n\text{-Butyl chloride}}{CH_3.CH_2.CH_2.CH_2Cl} \text{ and } \underset{sec\text{-Butyl chloride}}{CH_3.CH_2.CHCl.CH_3}$$

$$\frac{n\text{-Butyl chloride}}{sec\text{-Butyl chloride}} = \frac{\text{No. of 1°H}}{\text{No. of 2°H}} \times \frac{\text{reactivity of 1°H}}{\text{reactivity of 2°H}}$$

$$= \frac{6}{4} \times \frac{1 \cdot 0}{3 \cdot 8} = \frac{6}{15 \cdot 2} = \frac{28\%}{72\%}$$

In the above calculations, the ratio $\frac{\text{No. of 1°H}}{\text{No. of 2°H}}$ gives the probability factor. Larger the number of 1°H atoms, greater the probability of its abstraction.

Reactivity and Selectivity. By "selectivity" we mean the difference in rates at which the various classes of free radicals are formed ; a more stable free radical is formed faster. In its attack on alkanes the bromine atom is much more selective than the chlorine atom, its relative rate factor being 1600 : 82 : 1 as compared with 5·0 : 3·8 : 1 for chlorine. It is also much less reactive than the chlorine atom (only 1/250,000 as reactive towards methane). This is just one example of a general relationship : *in a set of similar reactions, the less reactive the reagent the more selective it is in its attack.*

Problem. *Calculate the relative amount of n-butyl bromide and sec-butyl bromide obtained on bromination of butane.* (Ans. 1·8% : 98·2%)

Inhibitors. The chlorination is slowed down by a small amount of oxygen for a period depending on the quantity of oxygen. Oxygen is believed to react with methyl radical to form a new radical.

$$CH_3^{\cdot} + O_2 \longrightarrow CH_3\text{—}O\text{—}O^{\cdot}$$

The new radical is much less reactive and can do little to continue the chain. Thus by combining with a $CH_3^{\cdot}$ radical one molecule of oxygen breaks the chain and prevents the formation of thousands of molecules of CH_3Cl. The reaction slows down tremendously. After all the oxygen molecules present have combined with methyl radicals, the reaction again proceeds at its normal rate.

A substance like oxygen that slows down or stops a reaction even though present in small amount is called an **inhibitor**. *The period during which inhibition lasts, and after which the reaction proceeds normally is termed* **inhibition period.**

(2) **Autoxidation.** Another example of a substitution reaction involving free radicals is autoxidation of organic compounds, *e.g.*, hardening of oil paints and varnishes, deterioration of rubber and plastics. This is photosensitised oxidation of these on exposure to air and sunlight. Traces of impurities present, *e.g.*, traces of metals, can act as initiators of chain reaction which then proceeds spontaneously. However, added peroxides act as powerful initiators. Mechanism for autoxidation of a hydrocarbon, RH is outlined below :

(*i*) $Ra\cdot + H\text{—}R \rightarrow RaH + R^{\cdot}$ (*Initiation step*)

(*ii*) $R\cdot + \underset{\text{oxygen (with diradical nature)}}{\cdot O\text{—}O\cdot} \rightarrow RO\text{—}O^{\cdot}$

(iii) $RO—O\cdot + H—R \rightarrow RO—OH + R\cdot$

(ii) and *(iii) are propagation steps.*

ADDITION REACTIONS

(1) **Addition of chlorine to tetrachloroethylene.** Addition of halogens to unsaturated compounds can follow an ionic or a radical mechanism depending upon the conditions of the reaction. In the vapour phase and in sunlight, the addition follows the radical mechanism almost entirely. Different steps involved in the addition of chlorine to tetrachloroethylene in presence of sunlight are :

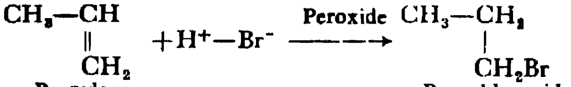
(i) $Cl—Cl \xrightarrow{h\nu} 2\ \cdot Cl$ *(Initiation step)*

(ii) $CCl_2{=}CCl_2 + \cdot Cl \rightarrow \cdot CCl_2—CCl_3$

(iii) $Cl—Cl + \cdot CCl_2—CCl_3 \rightarrow \cdot Cl + CCl_3—CCl_3$

(ii) and *(iii)* are *propagation steps.*

(2) **Addition of HBr to propylene.** In the presence of air or peroxides, addition of hydrogen bromide is abnormal as it takes place against the Markownikoff's rule. The action of peroxide to cause this abnormal addition is termed *Peroxide effect.*



$$\begin{array}{c} CH_3—CH \\ \| \\ CH_2 \end{array} + H^+—Br^- \xrightarrow{\text{Peroxide}} \begin{array}{c} CH_3—CH_2 \\ | \\ CH_2Br \end{array}$$

Propylene Propyl bromide

The mechanism of the peroxide effect, though not finally settled, appears to be a free-radical chain reaction, the peroxide generating the free radical is as follows :

(a) $\underset{\text{Peroxide}}{RO—OR} \longrightarrow \underset{\text{Free radicals}}{2RO\cdot}$

(b) $HBr + RO\cdot \longrightarrow ROH + Br\cdot$

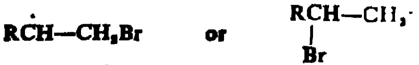
(c) $Br\cdot + \overset{\delta+}{RCH}{=}\overset{\delta-}{CH_2} \longrightarrow \underset{\text{Secondary free radical}}{R\dot{C}H—CH_2Br}$

(d) $R\dot{C}H—CH_2Br + HBr \longrightarrow RCH_2—CH_2Br + Br\cdot$, and so on.

Out of H· and Br· (from HBr), radical H·, being more unstable, adds first to the radical RO· obtained from the peroxide. Reason for separation of charge in $RCH{=}CH_2$ is the inductive effect on account of the electron repelling nature of R.

Free bromine atoms are *electrophilic* reagents due to their tendency to complete their octets and hence attack the olefin at its point of highest electron density in step (c).

The same can be predicted from the general rule : *Free-radical addition to a carbon-carbon double bond involves the intermediate formation of the more stable free radical,* their stability being in the order 3° > 2° > 1° > ·CH₃. For example, addition of Br· to $RCH{=}CH_2$ will give :



$$R\dot{C}H—CH_2Br \quad \text{or} \quad \begin{array}{c} RCH—CH_2\cdot \\ | \\ Br \end{array}$$

2° free radical 1° free radical
(Right) (Wrong)

It is a chain reaction in which (a) and (b) are the chain initiation steps, (c) and (d) are chain propagation steps Because of their low concentration bromine atoms obtained in (b) do not react with one another, instead add to the double bond of alkene whose concentration is massive.

Chain termination step is the chance contact of two free radicals. For instance, the secondary free radical formed in step (c) might unite with the $Br^{\cdot}$ formed in step (b) or (d) to produce a molecule of 1, 2-dibromoalkane. Amid several thousand molecules of 1-bromoalkane, the presence of this lone molecule would hardly be detectable.

Problem. Addition of $CHCl_3$ or CCl_4 to an alkene also occurs by free radical mechanism Write various steps for their addition to propylene.

Presence of peroxides affects the addition of hydrogen bromide only. This is because the bond energy of hydrogen chloride (H—Cl) is too high to break when free alkyl radical approaches it. In case of hydrogen iodide the H—I bond breaks easily but free iodine atom $I^{\cdot}$ is very unstable and gives iodine molecules, I_2 instead of adding.

(3) **Catalytic Reduction of Olefins.** Hydrogen is added to an olefin molecule in presence of finely divided nickel, palladium or platinum. The reaction is believed to proceed via the formation of free radicals as given below :

Molecules of the reactants (olefin and hydrogen) are adsorbed on the catalyst surface and dissociate into atoms or radicals. For example, hydrogen atoms and ethylene diradicals are produced during hydrogenation of ethylene.

$$H—H \longrightarrow 2H^{\cdot}$$

$$CH_2{=}CH_2 \longrightarrow H_2C—CH_2$$

Ethylene diradical

Ethylene diradicals and hydrogen atoms are stabilised by weak pairing of their unshared electrons by electrons of the metal surface forming a monomolecular layer.

Ethane is then produced by a collision between the ethylene diradical and a hydrogen atom, in two steps given below :

$$H_2C—CH_2 \xrightarrow{H^{\cdot}} H_3C—CH_2 \xrightarrow{H} H_3C—CH_3$$

Ethylene diradical   Ethyl radical   Ethane

ELIMINATION REACTIONS

Reactions involving fragmentation of radicals involving cleavage of carbon-carbon or carbon-hydrogen bonds resulting in the formation of smaller molecules may be considered as elimination reactions. For example

Pyrolysis of Hydrocarbons (Cracking). Ethane on pyrolysis gives a mixture of ethane, ethylene, methane and hydrogen. It is suggested that pyrolysis proceeds via the formation of free radicals. Ethane undergoes homolytic fission at high temperature to give two methyl radicals

$$CH_3—CH_3 \longrightarrow 2CH_3^{\cdot}$$

which react in either of the following ways :

(a) Methyl radical on collision with an ethane molecule to produce methane and ethyl radical

$$\underset{\text{Free methyl radical}}{CH_3^{\cdot}} + \underset{\text{Ethane}}{CH_3—CH_3} \longrightarrow \underset{\text{Methane}}{CH_4} + \underset{\text{Free ethyl radical}}{CH_3—CH_2^{\cdot}}$$

(*b*) Two methyl radicals unite in presence of a third molecule (*e.g.*, walls of the vessel) which absorbs the energy thus set free to produce ethane.

$$2CH_3^{\cdot} \longrightarrow \underset{\text{Ethane}}{CH_3—CH_3}$$

(*c*) The ethyl radicals produced in step (*a*) form ethylene by disproportionation.

$$\underset{\text{Two ethyl radicals}}{CH_3—CH_2^{\cdot}+CH_3—CH_2^{\cdot}} \longrightarrow \underset{\text{Ethane}}{CH_3—CH_3} + \underset{\text{Ethylene}}{CH_2=CH_2}$$

or

$$CH_3—CH_2^{\cdot} \rightarrow CH_2=CH_2 + H^{\cdot}$$
$$H^{\cdot}+CH_3—CH_3 \rightarrow CH_3—CH_2^{\cdot} + H_2$$
$$H^{\cdot}+H^{\cdot} \rightarrow H_2$$

A repetition of these reactions constitutes a chain reaction.

Exercise. From various steps indicated above for pyrolysis of ethane, write down various steps under the following heads :

(*i*) Initiation step,

(*ii*) Propagation steps, and

(*iii*) Termination steps.

POLYMERISATION

Vinyl polymerisation. Polymerisation of ethylene (a monomer) to form polyethylene (a polymer) involves three steps given below :

(*a*) *Chain Initiation step.*

Peroxide, etc., form a radical Ra· necessary for initiating the chain reaction.

(*b*) *Chain propagation steps.*

$$Ra^{\cdot} + \underset{\text{monomer}}{CH_2=CH_2} \rightarrow RaCH_2—CH_2^{\cdot} \xrightarrow{CH_2=CH_2}$$

$$\underset{\text{dimer}}{RaCH_2—CH_2—CH_2—CH_2^{\cdot}} \text{ or } Ra(CH_2)_3CH_2^{\cdot} \xrightarrow{\text{and so on}}$$

$$\underset{\text{polymer}}{Ra(CH_2)_{n-1}CH_2^{\cdot}}.$$

(*c*) *Chain termination steps.*

(*i*) $Ra(CH_2)_{n-1}CH_2^{\cdot} + {}^{\cdot}Ra \rightarrow Ra\,(CH_2)_n\,Ra$

(*ii*) $Ra(CH_2)_{n-1}CH_2^{\cdot} + {}^{\cdot}CH_2(CH_2)_{n-1}\,Ra \rightarrow Ra(CH_2)_{2n}\,Ra$

10. Eergy of Activation and Progress of Reaction.—According to the collision theory, necessary conditions for the reaction

$$Cl^{\cdot}+CH_3—H \longrightarrow H—Cl+CH_3^{\cdot} \quad ; \quad \Delta H = -4{\cdot}2 \text{ kJ}$$

to occur are :

(*i*) *A chlorine atom and methane molecule must collide.* Since chemical forces are of extremely short range, a hydrogen-chlorine bond can form only when two atoms are in close contact.

(*ii*) *To be effective, the collision must provide certain minimum amount of energy, called the* **energy of activation,** E_{act}. This is supplied by the kinetic energy of the moving particles. In the above reaction, energy of activation required is 18·74 kJ mol^{-1} and at 550K only about one collision out of 40 is sufficiently energetic.

(*iii*) *During collision the particles must be properly oriented.* For example, for the above reaction to occur the methane molecule must be so oriented at the instant of collision as to present a hydrogen atom to the full force of the impact. In the above case only about one collision in eight is properly oriented.

In general, a chemical reaction requires collisions providing sufficient energy (Energy of activation) and of proper orientation.

Potential energy changes taking place as the reaction progresses are seen more clearly in diagrams like Fig. 10·5. Progress of reaction is represented horizontally from reactants on the left to products on the right. Potential energy (*i.e.*, all energy except kinetic energy) at any stage of the reaction is represented by the height of the curve.

We start with potential energy valley on the left with methane molecule and chlorine atom (*reactants*). In addition to potential energy, the particles possess kinetic energy which varies since some move faster than others. On collision, some kinetic energy changes into potential energy. With this increase in potential energy the reaction starts and we move up the energy hill. With enough increase in potential energy ($=E_{act}=$16·8 kJ in this case), we reach the top of the hill and start down the far side of the energy hill. During descent more and more of potential energy changes into kinetic energy until we reach the potential energy valley on the right with methyl radical and hydrogen chloride molecule (*product*). The energy content of the products is less than the energy content of the reactants and the difference (ΔH) is given out as heat. A reaction of this type is termed exothermic reaction.

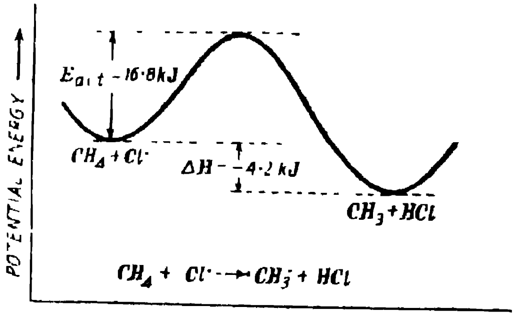


Fig. 10·5—Potential energy changes during progress of an exothermic reaction.

Rate of Reaction. Since a chemical reaction proceeds as a result of effective collisions of sufficient energy and proper orientation, the rate at which these collisions occur will determine the rate of reaction. The rate of effective collisions can be expressed as the product of three factors.

$$\text{Number of effective collisions per ml per sec} = \text{Total number of collisions per ml per sec} \times \text{Fraction of collisions having sufficient energy} \times \text{Fraction of collisions having proper orientation}$$

or

$$\text{rate} = \begin{matrix}\text{Collision}\\ \text{frequency}\end{matrix} \times \begin{matrix}\text{energy}\\ \text{factor}\end{matrix} \times \begin{matrix}\text{probability factor}\\ \text{(orientation factor)}\end{matrix}$$

The **collision frequency** depends on how closely the particles are crowded together, *i.e.*, its concentration or pressure. Heavier particles are generally larger ones. A heavy particle moves slowly and thus tends to decrease collision frequency but its large volume tends to increase collision frequency. These two factors thus tend to cancel out.

Energy factor depends on temperature and the energy of activation which is characteristic of each reaction.

Probability factor depends upon the geometry of the particles and the nature of reaction.

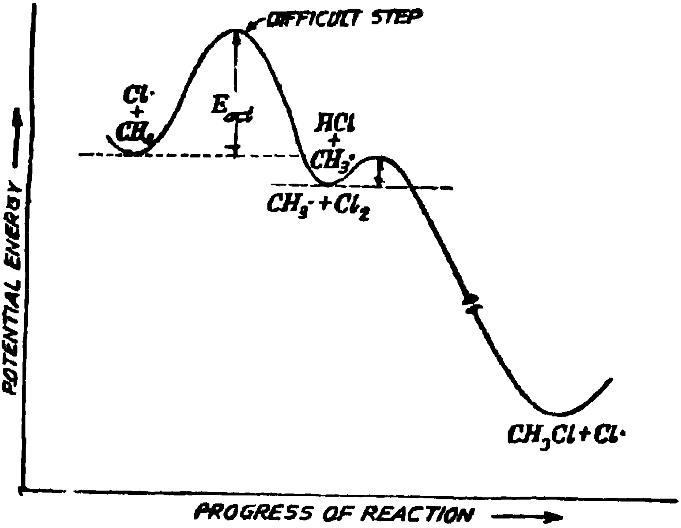


Fig. 10 6—Potential energy changes during progress of chlorination of methane. Formation of CH_3 is a difficult step.

Out of the two chain propagation steps in halogenation of methane

(1) $X + CH_4 \longrightarrow HX + CH_3\cdot$

(2) $CH_3 + X_2 \longrightarrow CH_3X + X\cdot$

step (1) is more difficult than step (2). Once formed, $CH_3\cdot$ will easily react with any of the halogens. It is how fast $CH_3\cdot$ radicals are formed that limits the rate of the overall reaction. ΔH for this step is -134, $-4\cdot2$, $+69$ and $+129\cdot7$ kJ respectively.

The order of reactivity of halogens

$$F_2 > Cl_2 > Br_2 > I_2$$

can be explained in terms of the difference in their E_{act} for the difficult step. Fluorination is very fast since fluorine atoms rapidly abstract hydrogen atoms from CH_4 ($E_{act}=5\cdot1$ kJ). E_{act} for chlorination and bromination is 16·9 and 77·8 kJ mol^{-1} respectively. Iodination does not take place because for iodine atoms it is virtually impossible to abstract hydrogen from CH_4 ($E_{act}=140\cdot2$ kJ mol^{-1}).

Structure of Methyl Radical We have come across a new species of free radicals. Let us see what is its shape. In methyl radical the carbon atom is in a state of sp^2 hybridisation. The three sp^2 orbitals lie in a plane mutually inclined at an angle of 120°. These three orbitals overlap with *s* orbitals of three hydrogen atoms to give methyl radical in which carbon atom lies at the centre of an equilateral triangle and three hydrogen atoms are at the three corners. Each bond angle is 120°. The odd electron lies in the remaining *p* orbital lying above and below the plane of three sp^2 orbitals (Fig. 10.8).

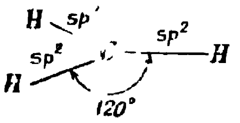


Fig 10.7—Methyl radical showing only the σ bonds

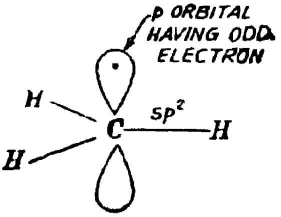


Fig 10.8—Methyl radical showing odd electron in *p* orbital above and below the plane of σ bonds.

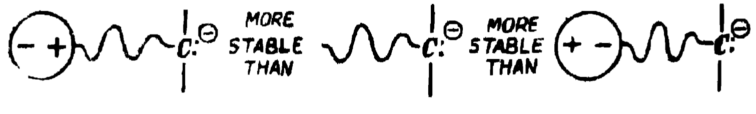
Problem Suggest electronic configuration to account for the fact that BF_3 is flat, triangular in shape whereas NF_3 molecule is pyramidal

11. Carbanions—We have learnt about the products of heterolysis—carbocation (R^+) or carbanions (R^-). Due to electronegativity of carbon a carbanion is an extremely strong base.

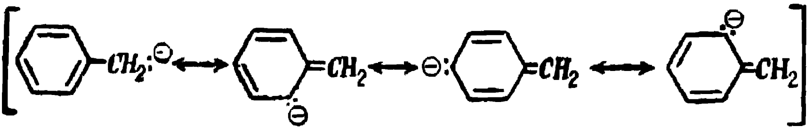
$$-\overset{|}{\underset{|}{C}}{}^{\ominus} + BH \rightleftharpoons -\overset{|}{\underset{|}{C}}-H + B^{\ominus}$$

Even with a moderate proton donor, the equilibrium is displaced completely to the right.

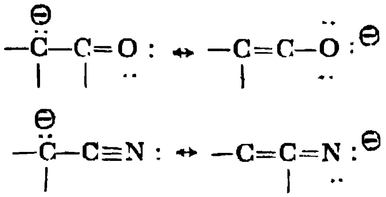
Carbanions are stabilised by both inductive and resonance effects. Being negatively charged, these are stabilised inductively by electron-withdrawing groups and rendered less stable by electron-releasing groups.



$C_6H_5CH_2:^{\ominus}$ is more stable than $CH_3CH_2:^{\ominus}$ because of the resonance stabilisation of the former as shown below :



Presence of $>C=O$ or $-C\equiv N$ adjacent to the carbanion is particularly good at stabilising. This is because in their case the stabilisation due to inductive effect of the electron-withdrawing group is combined with resonance stabilisation as shown below :

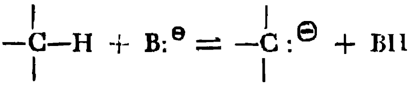


$$-\overset{\ominus}{\ddot{C}}-C=\ddot{O}: \leftrightarrow -C=C-\ddot{O}:^{\ominus}$$

$$-\overset{\ominus}{\ddot{C}}-C\equiv N: \leftrightarrow -C=C=\ddot{N}:^{\ominus}$$

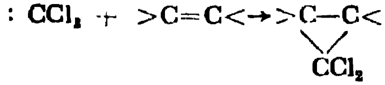
Hence most of the carbanions we shall come across as intermediates will be those derived from aldehydes, ketones, esters or cyanides.

A carbanion is readily formed in the reaction with a base, $B:^{\ominus}$ if the carbanion is sufficiently stabilised by any of the factors given above.



$$-\overset{|}{\underset{|}{C}}-H + B:^{\ominus} \rightleftharpoons -\overset{|}{\underset{|}{C}}:^{\ominus} + BH$$

12. Carbenes.—Carbenes are divalent carbon intermediates, *e.g.*, $:CH_2$ and $:CCl_2$. Since they need a pair of electrons to complete their outer shell, carbenes are likely to act as electrophiles. These add to a carbon-carbon double bond to give a cyclopropane.



$$:CCl_2 + {>}C=C{<} \rightarrow {>}\underset{CCl_2}{C-C}{<}$$

Some more reactions are given in properties of carbene (Chapter 14).

QUESTIONS

Essay Type :

1. What do you understand by the following terms .
(*i*) Homolytic fission or Homolysis,
(*ii*) Heterolytic fission or Heterolysis,
(*iii*) Carbanion,
(*iv*) Carbocation,
(*v*) Free radicals or Odd electron molecules,
(*vi*) Order of a reaction,
(*vii*) Rate determining step,
(*viii*) Zero order reaction ?

2. (*a*) What do you understand by electrophilic reagents and nucleophilic reagents ? Give examples of such reagents. (*Delhi B.Sc. Hons. 1973*)

(*b*) Arrange the following carbocations in the order of decreasing stability, giving reasons for your choices :

$$CH_3\oplus,\ C_2H_5\oplus,\ (CH_3)_2CH\oplus,\ (CH_3)_3C\oplus$$

(*Delhi B.Sc. Hons. 1973, 72*)

3. Write a short essay on reaction mechanisms giving appropriate examples of different types of reactions.

4. Explain the terms 'electrophilic' and 'nucleophilic' reagents. Discuss the mechanism of the addition of (*a*) HI, (*b*) Br_2, (*c*) HOCl to propene.

5. Write detailed mechanisms of each of the following reactions :

(*a*) Pyrolysis of ethane.

(*b*) Addition of HBr to propylene.

(*c*) Addition of HCN to acetaldehyde.

6. Make a list of four electrophilic reagents and write their actions with 2-methyl-2-butene, showing the mechanism.

7. Write short notes on :

(*a*) Reactivity and selectivity.

(*b*) Stability of free radicals and carbocations.

(*c*) Inhibitors.

8. Write electronic mechanisms for the following :

(*a*) Dehydration of 1-butanol.

(*b*) Dimerisation of isobutylene.

(*c*) Addition of isobutane to isobutylene.

9. (*a*) What are carbocations and carbanions ?

Explain why allyl cation is more stable than ethyl cation ?

(*b*) Give acceptable explanation for the observation that 2-chloro-3-methylbutane gives 3-methyl-2-butene as main product of the reaction on treatment with alcoholic potash. (*Delhi B.Sc. Hons. 1971*)

10. "Alkenes undergo electrophilic addition reaction whereas carbonyl compounds undergo nucleophilic addition. Taking propylene and acetaldehyde as examples, explain the above statement. (*Delhi B.Sc. Hons. 1976*)

11. Give the mechanism, stereochemistry and kinetics of *E1* and *E2* reactions in alkyl halides. (*Guru Nanak Dev B.Sc. 1977*)
(*See Chapter 17*)

Short Answer Type :

1. Give the mechanism for chlorination of methane. (*Delhi B.Sc. 1977 ; Madras 1976*)

2. Write note on : Mechanism of addition of bromine to ethylene. (*Delhi B.Sc. 1977*)

3. Write a short note on : Homolytic and heterolytic fission of a covalent bond. (*Nagpur B.Sc. 1974 Supp. ; Delhi B.Sc. Hons. 1977*)

4. Write a short note on : S_N1 reaction. (*Delhi B.Sc. Hons. 1977*)

5. What is the effect of introduction of an alkyl group on the stability of a carbocation ? (*Delhi B.Sc. Hons. 1977*)

6. Give mechanism of Dehydration of alcohols. (*Guru Nanak Dev B.Sc. 1977*)

7. Give mechanism of Dehydrohalogenation. (*Guru Nanak Dev B.Sc. 1977*)

8. Give the mechanism of Peroxide effect. (*Guru Nanak Dev B.Sc. 1977 ; Jabalpur 1976*)

9. Give the mechanism of alkylation of alkenes. *(Guru Nanak Dev B.Sc. 1977)*

10. Write what you understand by Unimolecular Nucleophilic Substitution S_N1. *(Guru Nanak Dev B.Sc. 1977)*

11. Explain electrophilic addition of halogens to ethylene. *(Jammu B.Sc. 1977)*

12. Account for the following :

t-Butyl chloride reacts with sodium hydroxide solution by the S_N1 mechanism while *n*-butyl chloride reacts by the S_N2 mechanism. *(Kerala B.Sc. 1975)*

13 Explain giving examples what are nucleophilic reagents. *(Jabalpur B.Sc. 1976)*

14. Account for the observation : *t*-butyl cation is more stable than *n*-butyl cation. *(Calicut B.Sc. 1975)*

15 Give one example where hydrolysis of an alkyl halide proceeds according to unimolecular (S_N1) mechanism and one example where it follows Bimolecular (S_N2) mechanism. *(Punjabi B.Sc. 1976 Supp.)*

16 How will you explain the following : Addition of bromine to an olefin gives a trans product *(Punjabi B.Sc. 1976)*

17. Give reason for the following : "Isobutene on hydration gives *t*-butyl alcohol." *(Madras B.Sc. 1976 Supp.)*

18. Write a short note on : Mechanism of nucleophilic addition to C=O. *(Madras B.Sc. 1976 Supp.)*

19 What products are formed on dehydration of 2-Butanol ? State the law which governs the elimination. *(Delhi B Sc. Hons. 1976)*

20 Assign the proper charges to the following and classify them as nucleophiles and electrophile :

(*i*) $:CCl_2$; (*ii*) $:CH_2CHO$; (*iii*) $H_3C—NH_2$. *(Delhi B.Sc. Hons. 1976)*

21. Classify carbonium ions. Give one example for each. Arrange them in their increasing order of stability and justify your arrangement. *(Andhra B.Sc. 1976)*

22. Write notes on the following :

(*i*) Homolytic and heterolytic bond fission.

(*ii*) Reaction of chlorine with methane and ethylene. *(Osmania B.Sc. 1978)*

23. Explain the following equations :

(*i*) $CH_3—CH=CH_2 \xrightarrow[775K]{Cl_2}$

(*ii*) $CH_3CHCl.CH_2CH_3 \xrightarrow[EtOH]{OH^-}$

24 Discuss the addition reaction of HBr with unsymmetrical alkene Discuss its mechanism. *(Delhi B.Sc. Hons. 1978)*

25. Discuss the addition of HCl in an α, β- unsaturated aldehyde. *(Delhi B.Sc. Hons. 1978)*

26. Write notes on :

(*a*) Carbocations. (*b*) S_N2 mechanisms. *(Bangalore B.Sc. 1978)*

27. Give an example through equation for (*a*) electrophilic addition (*b*) S_N1 reaction. *(Osmania B.Sc. 1978)*

28. Classify the following (as electrophilic, nucleophilic and free radical addition and substitution reactions) :

(*a*) $CH_4+Cl_2 \xrightarrow{h\nu} CH_3Cl+HCl$

(*b*) $CH_3Cl+NaOH \rightarrow CH_3OH+NaCl$. *(Osmania B.Sc. 1978)*

29. What are carbocations ? Mention three methods of their formation and discuss their stability. *(Andhra B.Sc. 1978)*

30. Discuss the mechanism of alkali hydrolysis of (*a*) Methyl bromide, (*b*) *tret*-Butyl bromide.

Bring out clearly the essential difference between the two reactions *(Andhra B.Sc. 1977)*

31. Give the mechanism of :

(*a*) Addition of bromine to ethylene. *(Andhra B.Sc. 1977 ; Calicut 1978)*

(*b*) Hydrolysis of esters using (*a*) acid, (*b*) alkali. *(Andhra B.Sc. 1976)*

32. Give an example of each of the following types of reactions bringing out clearly the essential differences between them :

(*a*) Electrophilic substitution

(*b*) Nucleophilic substitution

(*c*) Radical substitution. *(Andhra B.Sc. 1976)*

33. Write explanatory note on Types of elimination reactions. *(Andhra B.Sc. 1976)*

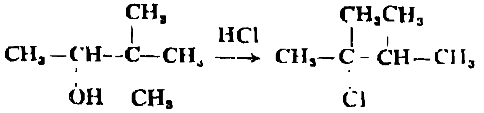
34. Explain why acetylene behaves like a nucleophile. *(Andhra B.Sc. 1976)*

35. Give an example for each of the following types of reactions :

(*a*) Electrophilic addition
(*b*) Nucleophilic addition
(*c*) Radical addition.

Bring out clearly essential difference between these reactions. *(Andhra B.Sc. 1976)*

36. Write mechanism that explains the course of the following reaction :



$$CH_3-\underset{OH}{CH}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3 \xrightarrow{HCl} CH_3-\overset{CH_3}{\underset{Cl}{C}}-\overset{CH_3}{CH}-CH_3$$

(Delhi B.Sc. Hons. 1980)

[**Hint.** Different steps involved are :

(*i*) Protonation of OH group.

(*ii*) Loss of a molecule of water.

(*iii*) Rearrangement of the Carbocation produced.

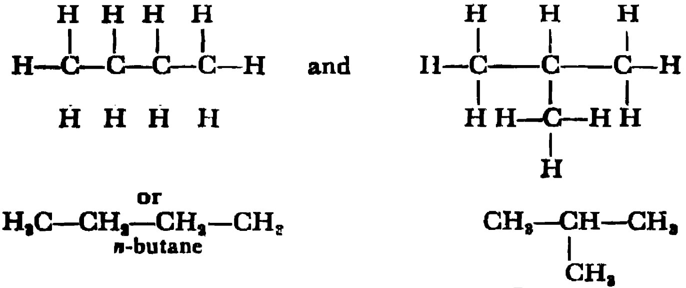
(*iv*) Nucleophilic attack by Cl⁻].

11

Stereochemistry

ISOMERISM

1. **What is Isomerism ?**—A molecular formula is not the last word about an organic compound. Just as a number of entirely different toys can be made with the same set of parts in a *Mechano* for children, the same set of atoms can be arranged in a number of ways to give more than one organic compounds. For example, C_4H_{10} is the molecular formula for butane. However, the 4 carbon atoms can be arranged in two different ways (in a straight or branched chain) as given below :



or

$H_3C—CH_2—CH_2—CH_3$ *n*-butane

$CH_3—\underset{\underset{CH_3}{|}}{CH}—CH_3$ Isobutane

Thus C_4H_{10} is the molecular formula of two different compounds *n*-butane and Isobutane.

Various organic compounds represented by the same molecular formula are called **Isomers** *or* **Isomerides** *while the phenomenon is termed* **Isomerism.**

2. **Types of Isomerism.**—Two common types of isomerism are :

(1) **Structural Isomerism.** When two or more compounds possess the same molecular formula but different structural formulae, they are said to exhibit structural isomerism.

(2) **Stereoisomerism.** Isomerism shown by compounds like lactic acid and 2-butene could not be explained easily. Here the isomerides have identical molecular and structural formulae and yet show isomerism. Such cases are, however, explained on the assumption that the different atoms, present in the molecule, occupy different positions in space. Thus different space models can be constructed to represent such isomerides.

The phenomenon exhibited by two or more compounds with the same molecular and structural formulae, but different spatial arrange-

ments of atoms or groups is termed stereoisomerism. The term was coined by Victor Meyer in 1888 from the Greek word *steros* meaning solid.

STRUCTURAL ISOMERISM

3. Structural Isomerism. Structural isomers differ in arrangement of their atoms. This difference may be due to the difference in the nature of chain of carbon atoms when the structural isomerism is termed *chain isomerism*. It may also arise from the different positions of the same substituent in the same chain when the structural isomerism is called *position isomerism*. Thus depending upon the nature of difference in structure, structural isomerism is of the following types.

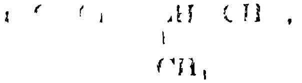
(1) Chain or Nuclear Isomerism. As stated before *n*-butane and isobutane are two structural isomers of butane C_4H_{10}. The difference of these isomers is due to the difference in the nature of carbon atom chain. In *n*-butane it is a straight chain whereas in isobutane it is a branched chain.

The isomers of pentane given below are also chain isomers.

(i) $H_3C-CH_2-CH_2-CH_2-CH_3$,

n-pentane *straight chain*

(ii)

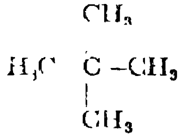


$H_3C-CH_2-\underset{\substack{|\\CH_3}}{CH}-CH_3$,

isopentane

(Branched chain with one tertiary carbon atom)

(iii)



$H_3C-\underset{\substack{|\\CH_3}}{\overset{\substack{CH_3\\|}}{C}}-CH_3$

neopentane

(Branched chain with one quaternary carbon atom)

(2) Position Isomerism. *Isomerism caused by different position of the same substituent in the same chain is termed position isomerism.*

For example

$CH_3CH_2CH_2I$ and CH_3CHICH_3.

n-propyl iodide, isopropyl iodide

or 1-iodopropane, or 2-iodopropane

oth have straight chain formulae but differ in the position of the alogen atom which is linked with the end carbon atom in the first ase and with the middle carbon atom in the other.

Similarly

$CH_2=CH-CH_2-CH_3$ and $CH_3-CH=CH-CH_3$

1-Butene, 2-Butene

th have straight chain formulae but differ in the position of the uble bond.

(3) Functional Isomerism. Monohydric alcohols are isomeric th ethers, the general formulae for both of these being $C_nH_{2n+2}O$. us ethanol C_2H_5OH is isomeric with dimethyl ether, $CH_3O.CH_3$ 1-propanol, C_3H_7OH is isomeric with ethyl methyl ether, $H_5O.CH_3$

This type of isomerism due to the presence of different ctional groups is called *Functional isomerism* and the isomers are med as *Functional isomers*.

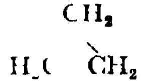
Some other examples of functional isomerism are

(i) [illegible] and CH_3COCH_3

[illegible] Acetone

both having [illegible] formula C_3H_6O

(ii) [illegible] and



Cyclopropane or Trimethylene

both having [illegible] formula C_3H_6

(4) **Metamerism.** It is the type of isomerism exhibited by members of the same homologous series due to the difference in the nature of alkyl groups attached to the polyvalent atom of the functional group. For example, there are three isomeric ethers represented by the molecular formula $C_4H_{10}O$ [illegible]

[illegible] $CH(CH_3)_2$

[illegible] Methyl [illegible] propyl ether

[illegible] represented by the [illegible]

[illegible] propyl ketone

[illegible] and alkyl [illegible] explain their [illegible] two isomeric

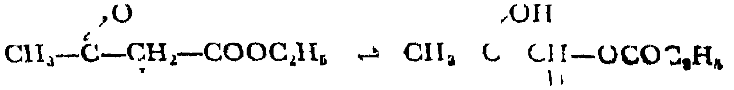
[illegible]

[illegible] constantly chang[illegible] *Tauto*[illegible] atom between

[illegible] keto [illegible]

[illegible] atom between the two polyvalent atoms [illegible]

[illegible] Acetoacetic ester gives the reactions of a keto compound and an unsaturated hydroxy compound. To explain its dual behaviour, it is assumed that it exists in two isomeric forms given below.

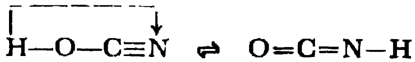


$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-COOC_2H_5 \rightleftharpoons CH_3-\overset{OH}{\overset{|}{C}}=CH-COOC_2H_5$$

Form I is constantly changing into the form II and *vice versa*. Thus it is a dynamic isomerism caused by the wanderings of a labile hydrogen atom which oscillates like a pendulum between two polyvalent atoms—carbon and oxygen.

Form I contains a keto group (>C=O) and is termed ***keto form***. Form II is called ***enol form*** due to the presence of an enol group (C=C—OH). Enols are compounds containing a double bond (C=C) as in alkenes and an OH group as in an alcohol. It is, therefore, known as **keto-enol tautomerism.**

(*iii*) Cyanic acid exhibits tautomerism and occurs as



$$H—O—C\equiv N \rightleftharpoons O=C=N—H$$

Cyanic acid gives rise to cyanates

Iso cyanic acid gives rise to iso-cyanates

The labile hydrogen atom oscillates between the polyvalent atoms—oxygen and nitrogen.

Difference between Tautomerism and Resonance. Tautomerism should be carefully distinguished from resonance as there is no point of similarity between the two. Some of the important points of difference between them can be enumerated as under :

(*i*) Tautomers involved in tautomerism are definite compounds whereas canonical forms of a resonance hybrid are only hypothetical and do not actually exist.

(*ii*) Tautomerism involves the wanderings of a labile hydrogen atom between two polyvalent atoms. Thus tautomers differ in atomic arrangement. On the other hand, contributing structures of a resonance hybrid have identical atomic arrangement. These differ only with respect to placement of electron on different atoms.

(*iii*) Tautomers are in dynamic equilibrium with each other shown by (⇌) sign between them. Since canonical forms of a resonance hybrid are only hypothetical, question of existence of any dynamic equilibrium between them does not arise. Resonance is indicated by a double arrow (↔) between its contributing structures.

(*iv*) One of the requisites for resonance to occur is that the molecule must be planar whereas there is no such requisite for tautomerism.

(*v*) Resonance is accompanied by increase in bond length of a double bond and shortening of a single bond while tautomerism does not involve any change in bond lengths.

(*vi*) Resonance results in stabilisation of the molecule by lowering its internal energy. There is no such effect in the case of tautomerism.

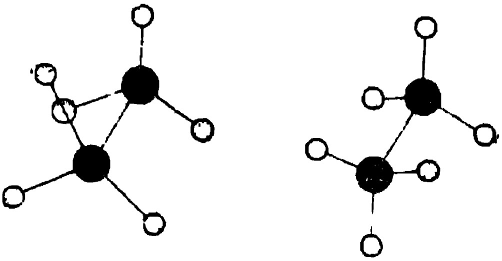
CONFORMATION

4. **Rotational Isomers or Conformations.**—Construct a ball-and-stick model of ethane molecule, $CH_3—CH_3$. You find two CH_3 groups are joined by a stick. If we allow one CH_3 group to rotate about this stick, we find that an infinite number of atomic

arrangements are possible depending upon the angles between two planes, one defined by a designated *C_1—H bond and the C_1—C_2 bond and the other defined by a designated C_2—H bond and the C_1-C_2 bond. This angle is termed **the Dihedral angle or the angle of torsion.**

Molecules capable of forming isomers by rotation about a single bond are termed **flexible molecules** and the isomers which differ only by rotation about one or more single bonds are termed **rotational isomers** or **conformations.**

Two extreme arrangements or conformations are shown in Fig. 11·1 and are known as the eclipsed and the staggered conformations. Look at the models in such a way that the back carbon is exactly covered by the front carbon and not seen. In the eclipsed conformation the three hydrogens attached to front carbon are exactly in front of those attached to the back carbon. In the staggered conformation all the six hydrogen atoms are clearly seen and appear symmetrically situated at maximum possible distances.



eclipsed *staggered*

Fig. 11·1—Two rotational isomers or conformations of ethane.

It has not been possible to separate the eclipsed and staggered conformations. This is because in ethane molecule there is free rotation about the single bond joining the two carbons. It is assumed that free, or at least rapid, rotation is possible around all the single bonds. Exceptions are only those molecules with very large groups attached which cannot pass by one another or when these are connected together by chemical bonds. For example, two forms of $CHBr_2$—$CHBr_2$ have been isolated at low temperatures. Collisions between molecules at low temperatures do not provide enough energy for interconversion.

However, in 1937 it was found experimentally that the entropy of ethane is somewhat lower than that calculated on the assumption that there is free rotation of methyl groups about the central C—C bond. This implies that there is somewhat reduced freedom of rotation. Subsequent experiments have confirmed that **staggered form of ethane is more stable than the eclipsed form which is associated with more energy** (=12·6 kJ mol^{-1}).

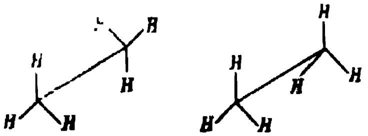
---

*Here C_1 indicates the carbon atom of the front CH_3 while C_2 indicates the carbon atom of the hind CH_3.

Let us understand why staggered form is more stable. When two unbonded atoms are brought closer they attract each other and the force of attraction is termed van der Waals forces. However, if these atoms are forced still closer together, they tend to repel each other. This repulsion is called **non-bonded interactions**. It raises the energy of the system and makes it less stable. In the staggered conformation the hydrogen atoms are as far apart as possible (internuclear H—H distance=3·1 Å) and non-bonded interactions between them are, therefore, minimum. The internuclear H—H distance in the eclipsed form is only 2·29 Å. Since the hydrogen atoms are closer here, the increased overlap between the non-bonded orbitals is repulsive. The magnitude of this repulsion per pair of hydrogen atoms is, however, small (=4·2 kJ mol^{-1}).

Ball and stick models are quite helpful for visualization of the relative positions of different atoms of these rotational conformations in space. Unfortunately, it is rather difficult to visualize the same from drawings in two dimensions. Some sort of abbreviations are, therefore, necessary. Two such abbreviations used for representation of conformations are :

(*i*) **Sawhorse drawings.** This is a three-dimensional convention which is simple and quite easy to draw. In these drawings we consider that we are viewing the molecule slightly from above and from the right and the lower left-hand carbon is always taken to be towards the front. Sawhorse drawings for staggered and eclipsed conformations of ethane are given in Fig. 11·2.

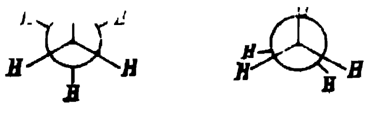


staggered *eclipsed*

Fig. 11·2—Sawhorse convention for showing staggered and eclipsed conformations of ethane.

(*ii*) **Newman Projection formulae.** In a Newman projection we view the C—C bond end on. The rearer carbon is represented by a point while the bonds linking the three other groups attached to this carbon are represented by three lines radiating from this point. The carbon atom situated farther away is represented by a circle and its three bonds represented by three lines radiating from the edge of the circle. Newman projections for the eclipsed and staggered forms of ethane are given in Fig. 11·3.

A look at the projections will show that a rotation of the front CH$_3$ group by 60° about the C—C axis converts the staggered conformation into the eclipsed one. If the rotation is continued further by another 60°, a new staggered conformation results.



staggered *eclipsed*

Fig. 11·3—Newman projections illustrating the staggered and eclipsed conformations of ethane.

Similarly, if the rotation is continued still further by 60°, a new eclipsed form is reached. Thus every time a staggered form is reached, potential energy of ethane decreases to minimum and again increases to maximum when the eclipsed conformation is obtained. A plot of potential energy of ethane *versus* degree of rotation of front CH_3 group for one complete rotation of 360° about the C—C bond is shown in Fig. 11·4.

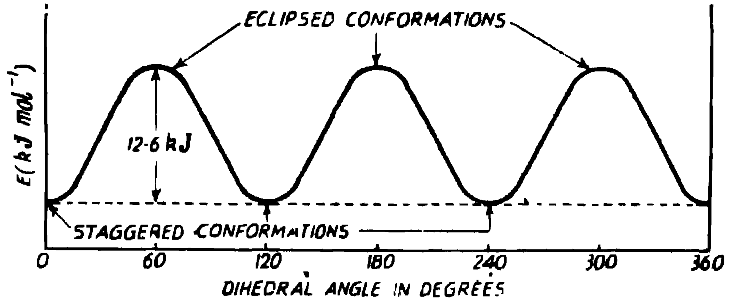
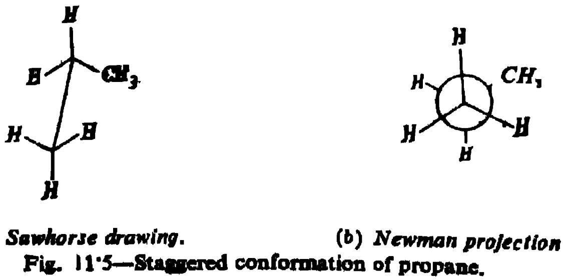


Fig. 11·4—Change in potential energy of ethane with degree of rotation about the C—C bond.

Thus there is an energy barrier of 12·6 kJ mol^{-1} in passing from one staggered conformation to another by rotation about the C—C axis.

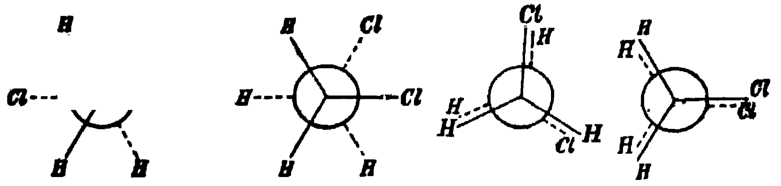
In propane the energy barrier to rotation is slightly higher (= 14·2 kJ mol^{-1}). Its most stable staggered conformation is shown in Fig. 11·5.



(*a*) *Sawhorse drawing.* (*b*) *Newman projection*

Fig. 11·5—Staggered conformation of propane.

Between these two conformations there is the less stable skew form. For example, in case of 1, 2-dichloroethane there are four conformations represented as under :

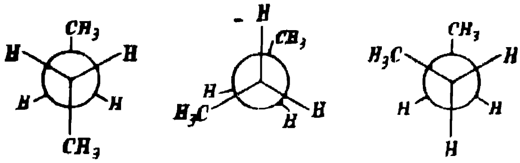


Trans or Staggered form (*Most Stable*)
Skew or Gauche form (*Less Stable*)
Eclipsed form (*Less Stable than Skew*)
Fully eclipsed form (*Least Stable*)

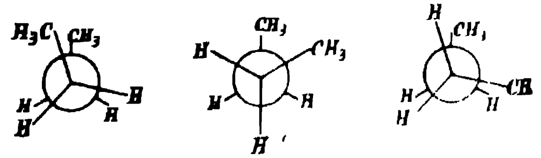
Fig. 11·6—Four conformations of 1,2-dichloroethane.

Although these conformers (conformation isomers) cannot be separated, they have been detected by infrared and Raman spectra.

Similarly, various conformations of *n*-butane obtained by rotating C_2 or C_3 through 360° in six steps (60° each time) are given below :



Completely staggered or Anti form (I)
Eclipsed form (II)
Skew or Gauche form (III)



Fully eclipsed form (IV)
Skew or Gauche form (V)
Eclipsed form (VI)

Fig. 11·7—Conformations of *n*-butane.

The energy changes taking place during rotation of C_2 or C_3 about C_2—C_3 bond resulting in the various conformations are shown

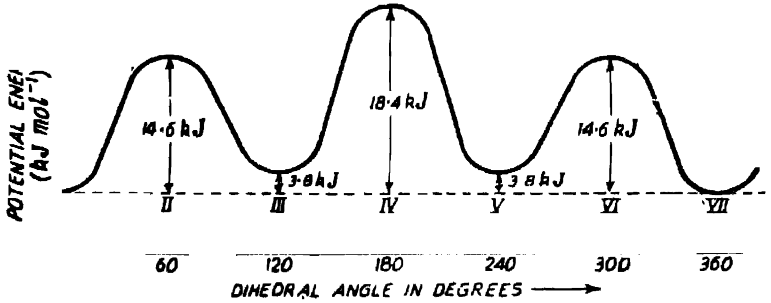


Fig. 11·8—Potential energy of butane as function of dihedral angle.

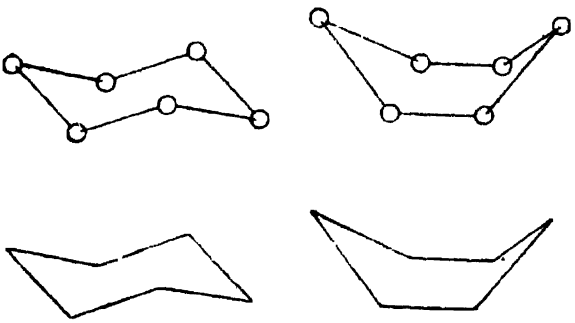
in the potential energy curve aganist the dihedral angle in **degrees in Fig. 11·8.**

The fully staggered form **I** is **the** most stable. It is slightly **more stable** than the skew or Gauche forms (III and V), difference of energy between them being 3·8 kJ mol^{-1}. Potential energy of **eclipsed** form (II and V) is 14·6 kJ mol^{-1} and that of fully **eclipsed** form (IV) is 18·4 kJ mol^{-1}.

These conformational isomers differ from one another only in spatial relationships of various atoms and are, therefore, a kind of *stereoisomers*. The two gauche forms (III and V) are termed **conformational enantiomers.** The staggered form I and the gauche form (III or V) are termed **cnoformatonal diastereomers** (see page 195).

5. **Conformations of Cyclohexane.**—Two conformations of cyclohexane are shown in Fig. 11·9 and are termed chair or 'Z' conformation and boat or 'C' conformation.

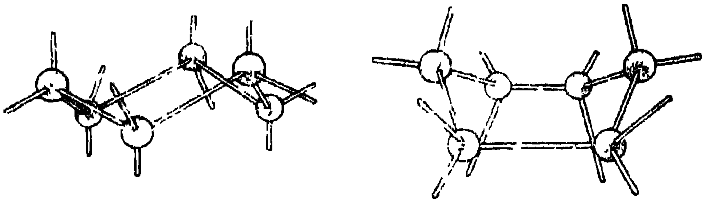
Interconversion of these two conformations involves only rotation about the carbon bonds but since the intermediate conformations through which the molecule passes are strained and hence less stable, there is an energy barrier between the two conformations though very small.



Chair or 'Z' Conformation Boat or 'C' Conformation

Fig. 11·9—Conformations of cyclohexane which are free of strain.

Chair conformation has been found to be more stable than the boat conformation by about 29 kJ mol^{-1}. A look at the models of the two conformations will reveal that in the chair conformation the hydrogen atoms are staggered whereas in the boat



Chair conformation Boat conformation

Fig. 11·10—Molecular models of chair and boat conformations.

conformation five pairs of hydrogen atoms approach each other closely. Repulsion between hydrogen atoms of each pair lowers the stability of boat conformation. Thus the difference in stability of the two conformations is due to crowding among hydrogen atoms of the boat conformation which results in non-bonded interaction (see page 174).

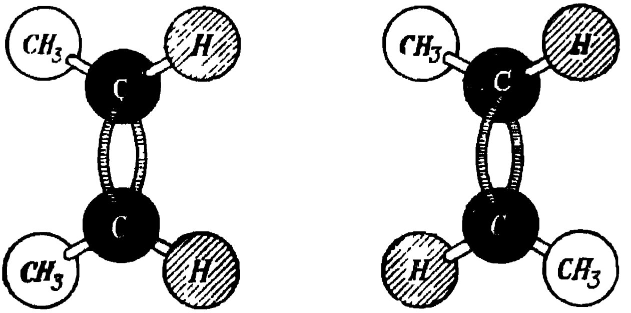
STEREOISOMERISM

6. Stereoisomerism.—*Isomerism exhibited by two or more compounds with the same molecular and structural formulae, but different spatial arrangements of atoms or groups is termed stereoisomerism.* It is of two types :

(1) **Optical Isomerism.** *See page* 189.

(2) **Geometrical Isomerism.** Examining the structure of 2-Butene we find that its atoms can be arranged in two different ways **I** and **II**. In **I** two CH_3 groups lie on the same side of the molecule while in **II** these lie on opposite sides of the molecule.

Conversion of **I** into **II** will involve rotation about the carbon-carbon double bond which is a combination of one σ bond and one π bond. The π bond is formed by the lateral overlapping of p orbitals which lie above and below the plane of σ orbitals. To pass from structure **I** to **II**, the molecule must be twisted so that p orbitals no longer overlap and the π bond is broken (*see* Fig. 11·12)



I
cis-2 Butene (*b.p.* 277K)

II
trans-2-Butene (*b p.* 274K)

Fig. 11·11— Space models of two *s*-Dimethylethylenes or 2-Butenes (*Geometrical isomers*).

167·2 kJ of energy are required for breaking a π bond and an insignificant number of collisions possess this much energy. Hence interconversion of **I** and **II** is extremely small, *i.e.*, rotation about the carbon-carbon double bond is hindered on account of this 167·2 kJ energy barrier. As a result of this hindered rotation the positions of different groups attached to the two carbon atoms are fixed in space.

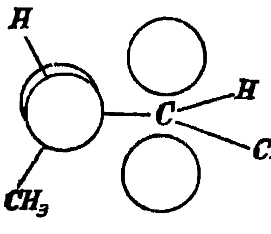
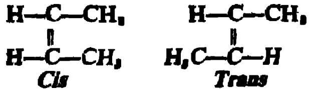


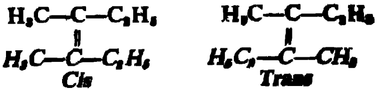
Fig. 11·12—Hindered rotation about carbon-carbon double bond. Rotation would prevent overlap of p orbitals and would result in breaking of π bond.

***The isomerism due to this in spatial arrangements of groups about the doubly bonded carbon atoms is called* Geometrical isomerism.** The isomer in which the similar groups lie on the same side is called the *cis isomer* (Latin, *cis*=on same side) and the other in which the similar groups lie on the opposite sides is called the *trans isomer* (Latin *trans*=across). Due to these *cis* and *trans* isomers, geometrical isomerism is called **Cis-Trans isomerism.**



$$\begin{array}{cc}\text{H—C—CH}_3 & \text{H—C—CH}_3\\ \| & \|\\ \text{H—C—CH}_3 & \text{H}_3\text{C—C—H}\\ \textit{Cis} & \textit{Trans}\end{array}$$

Dimethylethylenes
(Geometrical isomers)



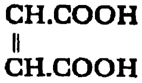
$$\begin{array}{cc}\text{H}_3\text{C—C—C}_2\text{H}_5 & \text{H}_3\text{C—C—C}_2\text{H}_5\\ \| & \|\\ \text{H}_3\text{C—C—C}_2\text{H}_5 & \text{H}_5\text{C}_2\text{—C—CH}_3\\ \textit{Cis} & \textit{Trans}\end{array}$$

Diethyldimethylethylenes
(Geometrical isomers)

Some other examples of compounds exhibiting geometrical isomerism are :

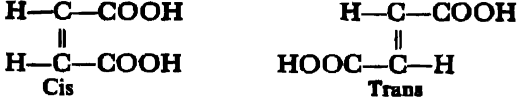
(*i*) **Isomerism of Maleic and Fumaric Acids.** Both maleic and fumaric acids have the same molecular formula, $C_4H_4O_4$. They differ in most of their physical properties and in some of their chemical properties.

Originally, they were thought as structural isomers and were, therefore, assigned different names. Later on it was shown that these are not structural isomers. They resemble in most of their chemical properties, *e.g.*, reduction, addition reactions, oxidation and formation of salts, or esters. Thus both acids have the same structure, as given in the margin.



$$\begin{array}{c}\text{CH.COOH}\\ \|\\ \text{CH.COOH}\end{array}$$

On the assumption that no free rotation is possible about a double bond, van't Hoff suggested that two spatial arrangements (*Geometrical isomers*) are possible for the above formula. These are :



$$\begin{array}{cc}\text{H—C—COOH} & \text{H—C—COOH}\\ \| & \|\\ \text{H—C—COOH} & \text{HOOC—C—H}\\ \text{Cis} & \text{Trans}\end{array}$$

Maleic acid which gives anhydride on heating is the *cis* variety and fumaric acid is the *trans* variety. Thus, we find that maleic and fumaric acids show *Geometrical isomerism.*

In the tetrahedral models, van't Hoff represented the double bond by placing the two tetrahedrons edge to edge (Fig. 11·13).

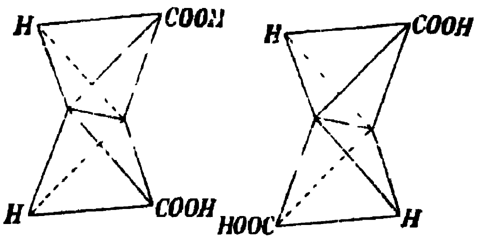
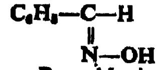


Fig. 11·13—Tetrahedral models for maleic and fumaric acids.

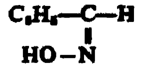
(*ii*) **Geometrical isomerism of oximes.** Just as two carbon atoms joined by a double bond (C=C) cannot rotate freely, a carbon atom and a nitrogen atom joined by a double bond (C=N) are also not capable of rotation. The positions of various groups joined to C=N are, therefore, fixed in space and the exhibit geometrical isomerism. Thus the aldoxime from b yde (C_6H_5CHO) exhibits geometrical iso and the two isomers have actually been isolated. These are :



$$\begin{array}{c} C_6H_5\text{—}C\text{—}H \\ \| \\ N\text{—}OH \end{array}$$

α-Benzaldoxime
(*syn*-form—m.p. 308K)

and



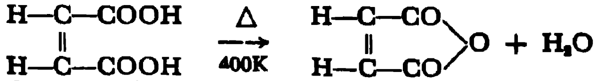
$$\begin{array}{c} C_6H_5\text{—}C\text{—}H \\ \| \\ HO\text{—}N \end{array}$$

β-Benzaldoxime
(*anti*-form—m.p. 303K)

The *isomer in which the H and OH groups* are on the same side is termed *cis-* or *syn-* while the other in which H and OH groups are on the opposite side is termed *trans-* or *anti-*.

Curiously enough the *anti-* form loses water more readily than the *syn-* variety when heated with acetic anhydride and phenyl cyanide (C_6H_5CN) is produced.

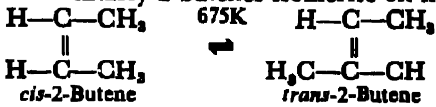
Properties of Geometrical Isomers. There is appreciable difference in the physical and chemical properties of the geometrical isomers. For example, melting point and stability of the *cis* isomer are lower than those of the *trans* isomer while its boiling point, solubility, density, dipole moment, refractive index and heat of combustion are higher. *Cis*-isomer of a dicarboxylic acid on heating readily loses a molecule of water to form the anhydride.



$$\begin{array}{c} H\text{—}C\text{—}COOH \\ \| \\ H\text{—}C\text{—}COOH \end{array} \xrightarrow[400K]{\Delta} \begin{array}{c} H\text{—}C\text{—}CO \\ \| \\ H\text{—}C\text{—}CO \end{array}\!\!\!>O + H_2O$$

Maleic acid (*cis*-) Maleic anhydride

Under suitable conditions (*e.g.*, application of heat, UV light or catalysts), geometrical isomers may be converted into each other. For example maleic acid changes into fumaric acid on heating above its melting point. Similarly 2-butenes isomerise on heating.

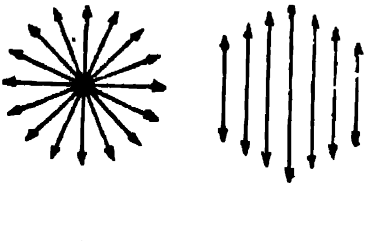


$$\begin{array}{c} H\text{—}C\text{—}CH_3 \\ \| \\ H\text{—}C\text{—}CH_3 \end{array} \underset{}{\overset{675K}{\rightleftharpoons}} \begin{array}{c} H\text{—}C\text{—}CH_3 \\ \| \\ H_3C\text{—}C\text{—}CH \end{array}$$

cis-2-Butene *trans*-2-Butene

OPTICAL ISOMERISM

7. **Polarized Light.**—According to the wave theory an ordinary ray of light is considered vibrating in all planes perpendicular to



(*a*) Unpolarized light (*b*) Polarized light

Fig. 11·14—Unpolarized and polarized lights.

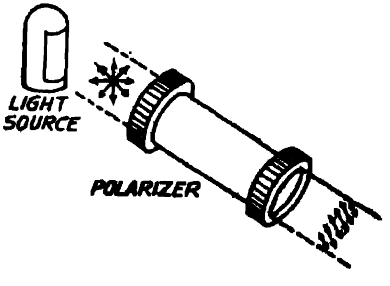


Fig. 11·15—Polarization of light.

its path of propagation. On passing a beam of monochromatic light (*e.g.*, yellow light from a sodium flame) through a crystal of Iceland spar or tourmaline, it splits up into two beams each vibrating in one plane only. The two rays formed have different refractive indices.

If a crsytal of calcite is split along one of its natural axes, and then the two halves are cemented together with Canada balsam, the emerging ray of light will be vibrating only in one plane. The ray of monochromatic light on passing through the first half is split up into two rays each vibrating in one plane only. One of the two newly formed rays suffers total internal reflection while the other passes on straight.

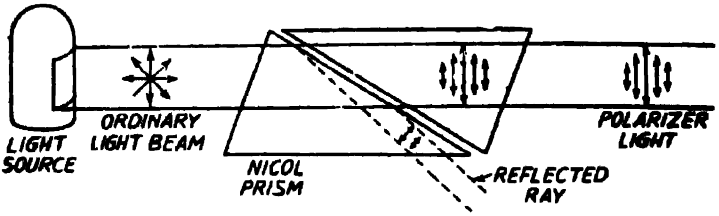


Fig. 11·16—Polarization of light with a Nicol prism.

The split crystal is called a Nicol prism* and light, whose vibrations are in one plane, is called polarized light. Suppose vibrations of a plane polarized light are taking place in the horizontal plane only then the vertical plane is termed the *plane of polarization.*

It is interesting to note what happens when a plane polarized light is passed through another Nicol prism. If the axis of the second

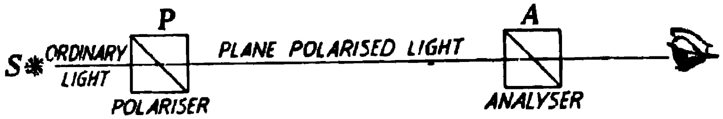


Fig. 11·17—Passing plane polarized light through another Nicol prism. Light reaches the eye when axes of *P* and *A* are parallel and no light reaches the eye when these are at right angles.

Nicol prism is parallel to that of the first, the polarised beam of light passes through and reaches the eye. If, however, the axis of the second Nicol prism is at right angle to the axis of the first, the polarized light is totally cut off due to total internal reflection and no light reaches the eye. In all intermediate positions of the second Nicol prism the polarized light is partially transmitted. Thus light of varying intensity reaches the eye. The second Nicol prism *A* is called the ***Analyser.***

8. **Optical Activity.**—Place two Nicol prisms between the source of monochromatic light *S* and the eye. Light passes through the first Nicol prism, *the polarizer* (*P*) and gets plane polarized. This plane polarized light passes through the second Nicol prism, *the analyser* (*A*) and reaches the eye. No light reaches the eye when the

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*Nicol prism is obtained by combining two prisms of Iceland spar suitably cut for the purpose. It is so named after the name of William Nicol of Edinburgh.

axis of the analyser is perpendicular to the axis of the polarizer.

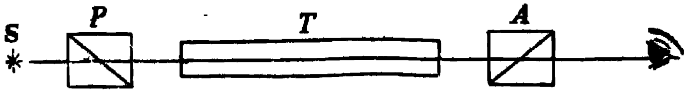

Fig. 11·18—Plane of polarization of plane polarized light is rotated by cane-sugar solution.

Now arrange the polarizer and the analyser for no light reaching the eye. Interpose a tube (T) filled with cane-sugar solution between the polarizer and the analyser, some light is visible. The analyser has to be rotated a little in order to get the original position of no light reaching the eye.

What has happened which made light visible on the right? Neither the polarizer nor the analyser has moved. This is possible only if the plane of polarization is rotated. This shows that cane-sugar solution has rotated the plane of polarization.

Substances of the type of cane-sugar which can rotate the plane of polarization of light are called *optically active* while the phenomenon is called **Optical activity**. Substances which rotate the plane of polarization of light towards the right are called **dextro-rotatory** whereas those which do so towards the left are termed **laevo-rotatory**.

The instrument used for measuring the angle of rotation of a plane polarized light is called a *polarimeter*. It has been found that the magnitude of rotation depends on a number of factors. For example,

(*i*) Nature of the compound.
(*ii*) Concentration of the solution.
(*iii*) Thickness of the layer traversed by polarized light.
(*iv*) Nature of the solvent.
(*v*) Wavelength of the light used.
(*vi*) Temperature of the solution.

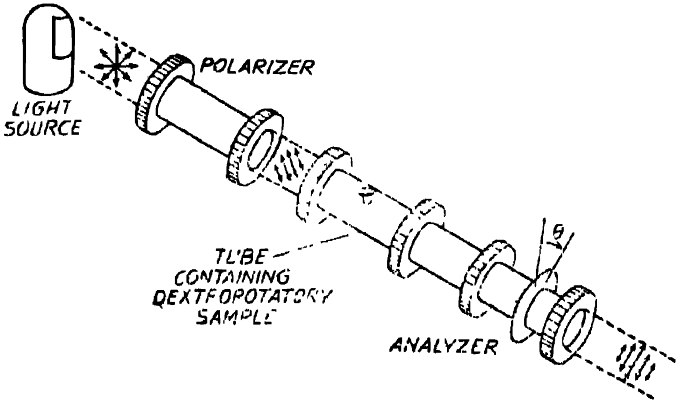

Fig. 11·19—Polarimeter.*

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*Refer to any book on Physical Chemistry for construction and working of a polarimeter.

The rotatory power of a given solution is usually expressed as **specific rotation**—*angle of rotation* (α) *produced by one decimetre* length of solution having one gram of the substance per cm^3. The measurement is carried out at temperature T kelvin using sodium light (the D line).

$$\text{Specific rotation} = \frac{100 \times \text{Observed angle of rotation, } \theta}{\text{Length in decimetres} \times \text{Grams of substance present in 100 cm}^3 \text{ of solution}}$$

$$\text{or} \qquad \left[\alpha\right]_D = \frac{100 \times \theta}{l \times c}$$

Molecular rotation is the product of specific rotation and molecular mass.

9. **Optically Active Substances.**—Optically active substances first discovered were all inorganic substances, *e g.*, quartz, some rock crystals, etc. Later on it was found that crystals of potassium chlorate, potassium bromate and sodium periodate were also optically active. Optical activity in their case is due to their *crystal structure* and disappears as soon as the solid is fused or dissolved in a solvent. A few organic compounds also show optical activity due to their crystal structure only, *e.g.*, benzil ($C_6H_5CO.CO.C_6H_5$).

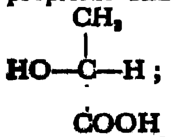
In 1815 Biot observed for the first time that certain organic compounds like sugar, tartaric acid, camphor and turpentine were optically active in the liquid or solution state.

It has been found that in order to exhibit optical activity, a compound must be **chiral** (possess handedness, from the Greek word *cheir* meaning hand). Your left hand is a mirror image of the right hand and the two are not superposable. It is a chiral object. A chiral molecule can be defined as *one that is not superposable on its mirror reflection.*

Compounds which are mirror images of each other and are not superposable are termed **enantiomers** (from the Greek words : *Enantio*=opposite ; *Meros*=part) and the phenomenon is described as **enantiomerism**. Enantiomers resemble each other in physical properties except that they rotate the plane-polarised light in opposite direction.

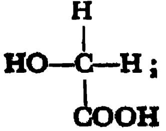
Organic compounds exhibit the property of enantiomerism only when their molecules are chiral. Most chiral compounds have a **chiral centre** which is *an atom* (usually carbon) *bonded to four different atoms or groups.*

The moment any two of the four atoms or groups become identical, the carbon atom is no longer chiral and optical activity disappears. For example, lactic acid is optically active while glycollic, propionic and isobutyric acids are not optically active.



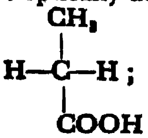
$$\begin{array}{c} CH_3 \\ | \\ HO\!-\!C\!-\!H \\ | \\ COOH \end{array}$$

Lactic acid
(Contains a chiral carbon atom)



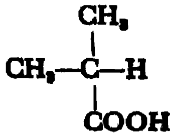
$$\begin{array}{c} H \\ | \\ HO\!-\!C\!-\!H \\ | \\ COOH \end{array}$$

Glycollic acid



$$\begin{array}{c} CH_3 \\ | \\ H\!-\!C\!-\!H \\ | \\ COOH \end{array}$$

Propionic acid

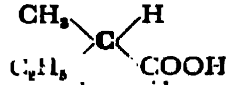


$$\begin{array}{c} CH_3 \\ | \\ CH_3\!-\!C\!-\!H \\ | \\ COOH \end{array}$$

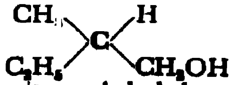
Isobutyric acid

(Do not contain chiral carbon atoms)

Iso-valeric acid and *iso*-amyl alcohol both contain a chiral carbon atom (shown black) and are optically active.



iso-valeric acid



iso-amyl alcohol

10. Symmetry Elements and Chirality.—Chiral molecules can be recognized by the presence of a *single* chiral centre. Another method for the same is to look for the presence of certain symmetry elements. For example, molecule will not be chiral if it possesses (*i*) a plane of symmetry designated by σ, (*ii*) a centre of symmetry (symbolised by *i*) or (*iii*) any *n*-fold (where *n* is an even number) alternating axis of symmetry (symbolised by C_n or S_n). The latter two elements of symmetry are beyond the scope of this book and we will depend only on our ability to recognize the presence or absence of the plane of symmetry to decide about the existence or non-existence of chirality in most of the molecules we come across.

A plane which divides an object into two identical halves is called **plane of symmetry**. A ball can be divided by a plane into two identical halves. It is a *non-chiral* or *achiral* object. No plane can divide a hand into two identical halves, *i.e.*, it has no plane of symmetry. It is chiral.

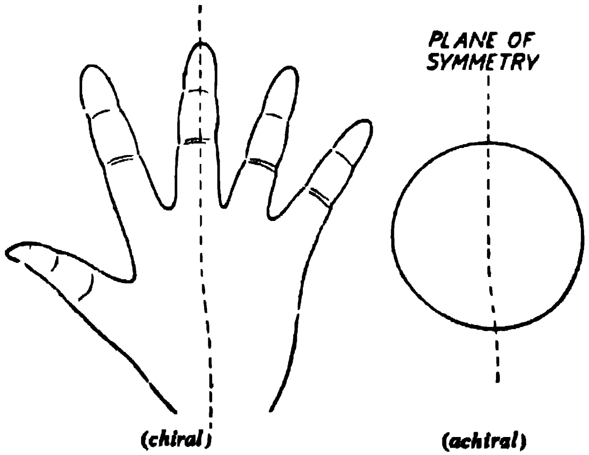


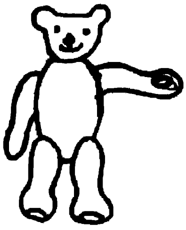
Fig. 11·20—Chiral and achiral objects.

A teddy bear may be a chiral object or an achiral one depending upon its stance, as shown on the next page.

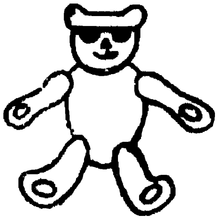
Asymmetric and Chiral molecules. The term *asymmetric* denotes absence of any symmetry. An object or molecule is asymmetric if it has no element of symmetry (*i*, σ, C_n or S_n)

The term *chiral* (handedness) denotes absence of all symmetry except (C_n) where *n* > 1. This *n*-fold axes of symmetry term has been adopted to define the structural features essential for a substance to be optically active.

All asymmetric molecules are chiral. However some symmetric molecules are also chiral when their symmetry is limited to their rotation axes (C_n). Hence a chiral molecule may not necessarily be asymmetric. Chiral objects are also called *dissymetric*. Substances which are not chiral are termed *achiral*



Teddy pointing
Chiral



Teddy sunbathing
Non chiral or achiral

11. Optical Isomerism.— Optically active substances, like lactic acid, are found to exist in three or more isomeric forms These isomers resemble one another in their chemical reactions and most of their physical properties but differ in their optical properties, *e g.*, in their behaviour towards polarized light. The isomers are called *optical isomers* whereas the phenomenon is known as *optical isomerism*.

To explain the existence of optical isomers, **Le Bell** and **van't Hoff** assumed in 1874 *that the carbon atom lies at the centre of a regular tetrahedron towards the four corners of which its four valency bonds are directed.* This view has further been supported by X-ray studies. Four different groups or atoms attached to a carbon atom give rise to optical activity. *Optical isomerism is due to different spatial arrangement of those four different atoms or radicals in the molecule.*

12. Optical Isomers of Lactic Acid.—Thus spatial arrangement of various groups in lactic acid can be represented in two ways (Fig. 11·21). These two models are not superimposable and are related to each other like an object and its mirror image or the right and the left hand.

A third optically inactive variety results when the *dextro-* and the *laevo-* varieties are present in equal quantities. It is called ***Racemic mixture*** or (±) ***lactic acid*** (Latin, *racemic* = mixture of equal components).

Now we can account for the existence of three lactic acids :

(*i*) *dextro*-lactic acid (m.p. 299K),

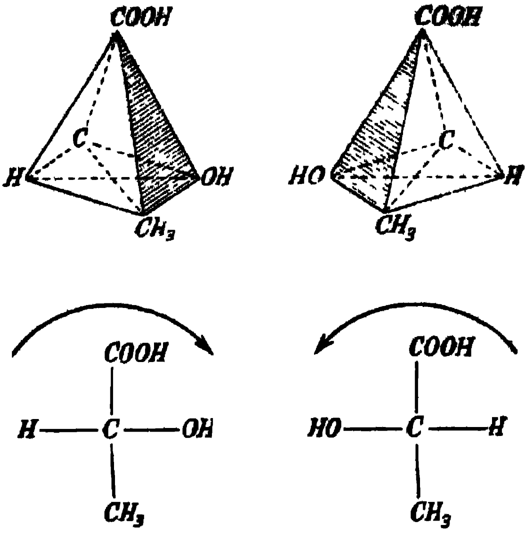
(*ii*) *laevo*-lactic acid (m.p. 299K), and

(*iii*) *racemic*-lactic acid (m.p. 291K).

Ordinary lactic acid present in sour milk or manufactured by fermentation or synthetic methods is racemic mixture and, therefore, inactive.

Dextro-rotatory lactic acid may be obtained from meat extract and is also known as sarcolactic acid (Greek ; *sarcos* =flesh). With muscular activity glycogen present in muscles breaks down to give sarcolactic acid. During rest sarcolactic acid is converted back to glycogen. Fatigue is due to accumulation of sarcolactic acid in muscles.

Laevo-rotatory lactic acid may be obtained by the fermentation of sucrose by *Bacillus acidi laevolactiti*.

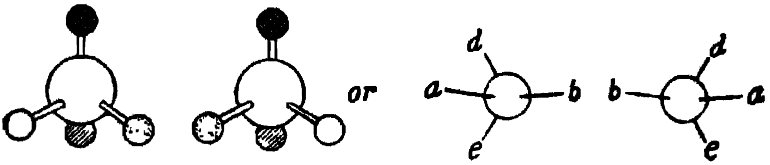


I
Dextro-rotatory or
(+) lactic acid

II
Laevo-rotatory or
(−) lactic acid

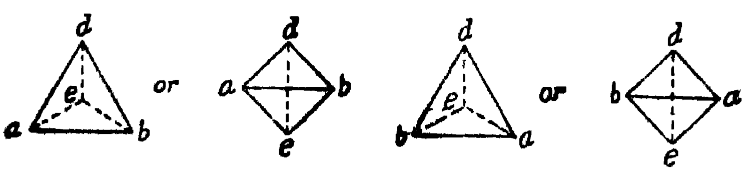
Fig. 11·21—Optical isomers of lactic acid.

Non-identical mirror images of a compound in which a carbon atom is attached to four different groups *a*, *b*, *d* and *e* [*e.g.*, (+)- and (−) lactic acid] can be represented in different ways, *e.g.*, by molecular models, by tetrahedra or perspective formulae and by projection formulae as shown below :

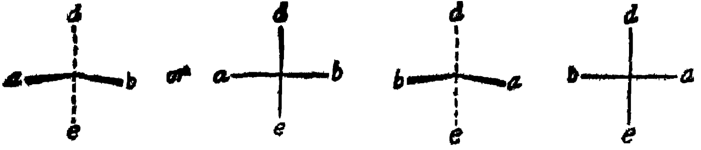


(Molecular models)

(Projection formulae)



(Perspective formulae or tetrahedra)



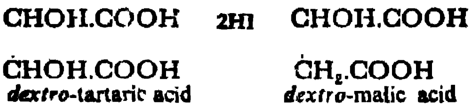
(Fischer Projection formulae)

Fig. 11·22—Representation of non-identical mirror images.

In a projection formula the chiral carbon atom is understood to be located where the lines cross. Chemists have agreed that in such a diagram *the horizontal lines represent bonds coming towards us out of the plane of the paper, whereas the vertical lines represent bonds going away from us behind the plane of the paper.*

In testing the superimposability of two of these flat, two-dimensional representations of three-dimensional objects, we may slide these formulae or rotate them *but must not remove them from the plane of the paper.*

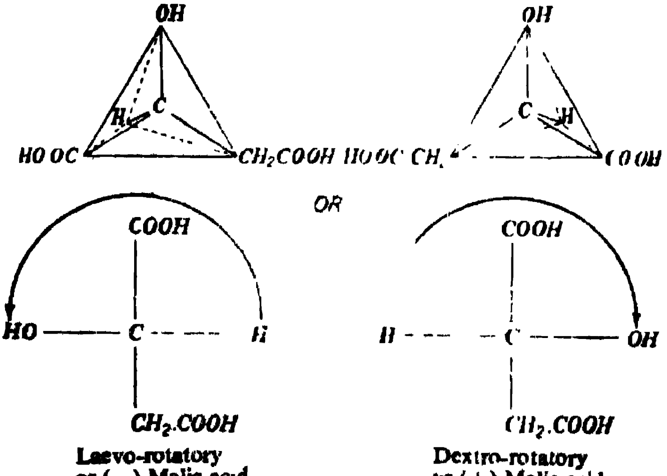
13. Optical Isomers of Malic Acid.—Malic acid molecule contains one chiral carbon atom and due to this exhibits optical isomerism. It exists in three isomeric forms—dextro, laevo and racemic. Malic acid obtained from natural sources is laevo. Synthetic malic acid is racemic or (±). Dextro-malic acid can be prepared by careful reduction of dextro-tartaric acid with concentrated hydriodic acid.



$$\begin{array}{c}CHOH.COOH\\ |\\ CHOH.COOH\end{array} \xrightarrow{2HI} \begin{array}{c}CHOH.COOH\\ |\\ CH_2.COOH\end{array}$$

dextro-tartaric acid *dextro*-malic acid

Dextro-malic acid may also be obtained from the *laevo*-isomer by means of *Walden inversion* (*see* page 202).



Laevo-rotatory or (—) Malic acid

Dextro-rotatory or (+) Malic acid

Fig. 11·23—Optical isomers of Malic acid.

14. Optical Isomers of Tartaric Acid.—Tartaric acid has two chiral carbon atoms each linked to the same four different groups, *viz.*, —OH, H, —COOH and —CH(OH)COOH.

The spatial arrangement of various groups in tartaric acid can be represented in three ways.

Corresponding to these different spatial arrangements, tartaric acid can exist in different forms (all of which are known) as given below.

(*i*) **dextro-Tartaric acid** which rotates the plane of polarization of light to the right. The rotation due to the upper half is strengthened by one due to the lower half. It has no plane of symmetry.

Acid obtained from natural sources, *e.g.*, tamarind and grapes, is of dextro- variety.

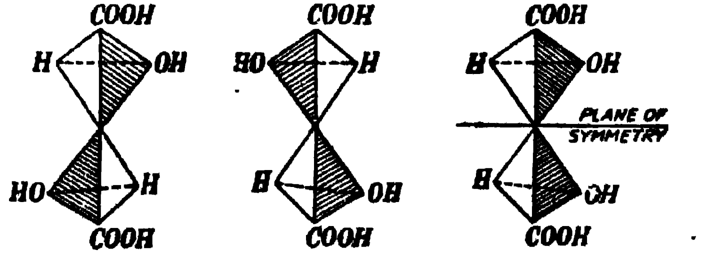
(*ii*) **laevo-Tartaric acid** is a mirror image of the above and rotates the plane of polarization of light to the left. Here again rotation due to the two halves is superimposed. This also has no plane of symmetry.

It does not occur in nature and is prepared by resolving the racemic acid.

(*iii*) **racemic-Tartaric acid** is a 50-50 mixture of the above two varieties and is hence inactive. It can, however, be resolved into the active constituents, *viz.*, *dextro-* and *laevo-varieties*. It is, therefore, inactive by external compensation

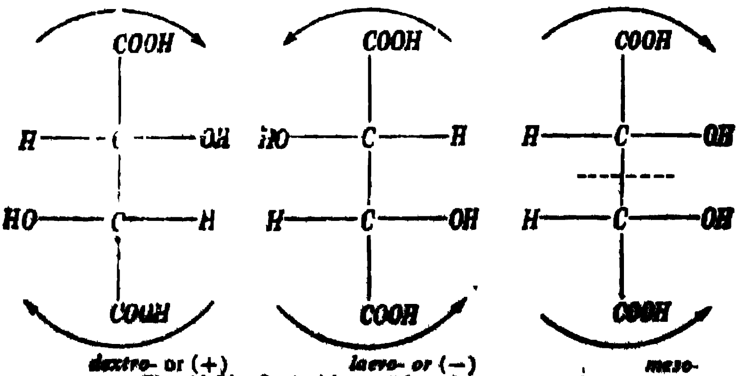
Synthetic acid is always inactive being either racemic or a mixture of racemic and the meso- varieties given below. Racemic acid mixed with meso- variety is also obtained when dextro- or laevo-acid is heated with water at 443K in a sealed tube or when boiled with concentrated caustic soda solution.

(*iv*) **meso-Tartaric acid** is the inactive variety as the rotation of upper half is compensated by the rotation due to the lower half



dextro- or (+) *laevo-* or (−) *meso-*

Or



dextro- or (+) *laevo-* or (−) *meso-*

Fig. 11·74—Optical isomerides of tartaric acid.

(being in opposite direction). It cannot be resolved into active constituents. It is, therefore, inactive by internal compensation. Unlike dextro- and laevo-varieties it has a plane of symmetry.

It does not occur in nature. It is, however, obtained along with racemic mixture by different methods given above.

Various physical constants of the isomers are :

Name	*M. Pt.*	*Density*	$[\alpha]_D$	*Crystal form*	*Solubility at 293K*
Dextro-	443K	1·760	+12°	prisms	139
Laevo-	443K	1·760	−12°	prisms	139
Racemic-	479K	1·666	0	rhombic	206
Meso-	413K	1·697	0	plates	125

15. Optical Isomers of Substituted Allenes.—Possibility of enantiomerism in substituted allenes of the type $abC{=}C{=}Cab$ was recognised by van't Hoff as early as 1875. It was, however, verified experimentally only in 1935.

In a substituted allene having cumulated double bonds, the two π bonds are perpendicular to each other (Fig. 11·25). The four substituents *abab* attached to the allenic carbon atoms lie in intersecting planes and the two structures I and II are non-superimposable. These being related to each other as object and mirror image are enantiomers. Chiral axis in I and II can be represented by two arrows as follows :

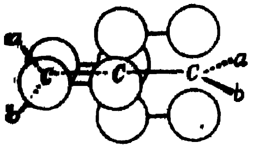
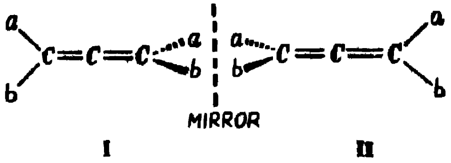
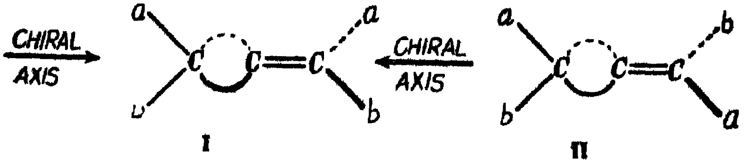


Fig. 11·25—π bonds in allene are perpendicular to each other.



These two molecules (object and its mirror image) being non-superimposable are chiral even though they do not possess a chiral centre.

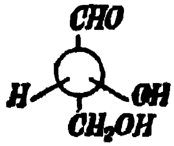


CONFIGURATION

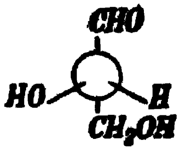
16. Specification of Configuration.—*The arrangement of atoms that characterises a particular stereo-isomer is called its con-*

figuration. Using the test of superimposability, we conclude that there are two stereo-isomeric lactic acids as given on page 190. One rotates the plane of plane-polarized light to the right and is named dextro or (+). The other which rotates the plane of plane-polarised light to the left is termed laevo or (−). Does the (+) isomer have configuration I or II ? How to assign configuration and how to specify a particular configuration in some simple and convenient way without drawing its picture ?

(*a*) **Dee(D) and Ell(L) Notation.** Since it is convenient to designate the configuration of a molecule by a symbol, a system involving letters D and L was adopted for the purpose. The standard chosen for relative configuration of carbohydrates was glyceraldehyde. Absolute configuration of (+)- and (−)-glyceraldehyde is known to be :



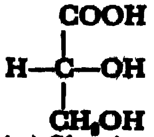
(+)-glyceraldehyde
I



(−)-glyceraldehyde
II

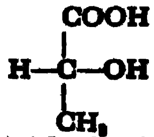
Glyceraldehyde (I) with OH group on right side of the molecule is denoted as D-glyceraldehyde while the other (II) with OH group on the left side of the molecule is termed L-glyceraldehyde. The system may be extended to other optically active compounds with some additional rules.

For hydroxy acids the convention is to draw the molecule with carboxyl group at the top. (−)-Glyceric acid and (−)-lactic acid have the same absolute configuration as D-glyceraldehyde, so they both belong to D family.



$$\begin{array}{c} COOH \\ | \\ H-C-OH \\ | \\ CH_2OH \end{array}$$

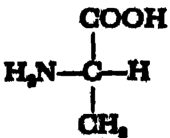
D-(−)-Glyceric acid



$$\begin{array}{c} COOH \\ | \\ H-C-OH \\ | \\ CH_3 \end{array}$$

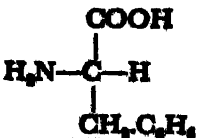
D-(−)-Lactic acid

All naturally occurring α-amino- acids have a configuration with —NH_2 group on the left side and by analogy to L-glyceraldehyde belong to Ell(L)-family irrespective of their direction in which they rotate the plane of polarized light.



$$\begin{array}{c} COOH \\ | \\ H_2N-C-H \\ | \\ CH_3 \end{array}$$

L-(+)-Alanine



$$\begin{array}{c} COOH \\ | \\ H_2N-C-H \\ | \\ CH_2.C_6H_5 \end{array}$$

L-(−)-Phenylalanine

To decide the configuation of any given molecule proceed as follows :

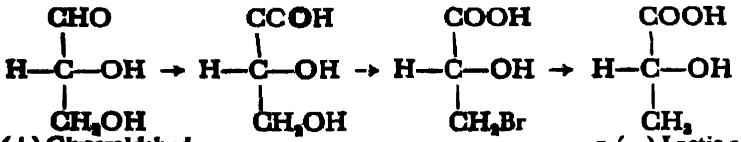
(*i*) Hang it from the most oxidised carbon atom. For example, in glyceraldehyde keep CHO group at the top.

(*ii*) The group with carbon atom forming a part of chain is to be kept away from you. For example, in glyceraldehyde group CH_2OH will be at the bottom.

(*iii*) The remaining two groups should be projecting towards you.

Now if the OH or NH_2 group is towards your right, it has the D-configuration and if it is on your left, it has the L-configuration.

Experimental Correlation of Configuration. It is important to understand how we relate the configuration of one optically active compound with another of established configuration. We shall illustrate it by transformation of D-(+) glyceraldehyde into D-(−) lactic acid.



$$\text{H}-\underset{\text{CH}_2\text{OH}}{\overset{\text{CHO}}{\text{C}}}-\text{OH} \rightarrow \text{H}-\underset{\text{CH}_2\text{OH}}{\overset{\text{CCOH}}{\text{C}}}-\text{OH} \rightarrow \text{H}-\underset{\text{CH}_2\text{Br}}{\overset{\text{COOH}}{\text{C}}}-\text{OH} \rightarrow \text{H}-\underset{\text{CH}_3}{\overset{\text{COOH}}{\text{C}}}-\text{OH}$$

D-(+) Glyceraldehyde D-(−) Lactic acid

Since configuration of lactic acid thus obtained corresponds to that of D-(+) glyceraldehyde, lactic acid has D-configuration. Further, since the acid obtained is laevorotatory, it is D-(−) lactic acid.

Similarly, L-(−) glyceraldehyde gives L-(+) lactic acid as a result of corresponding reactions.

Notes. 1. D- and L- refer to the absolute configuration (a three-dimensional structure).

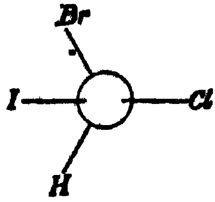
2. (+) and (−) refer to the rotation of the plane of polarized light, a physical property.

In the past, *d* (=*dextro*) and *l* (=*laevo*) were used instead of (+) and (−).

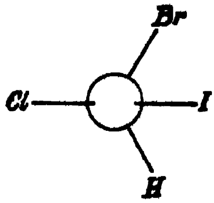
(*b*) **R and S Notation (Rectus and Sinister System).** Cahn, Ingold and Prelog proposed a scheme of nomenclature using the prefixes R and S. The two steps involved are :

Step I. *Following a set of sequence rules* (*see Sec. 17*), *a sequence of priority is assigned to the four different groups of atoms attached to the chiral carbon atom.* One criterion of priority is based on atomic numbers—*an atom with higher atomic number gets higher priority.*

For example, in the case of bromochloroiodomethane given below :



I

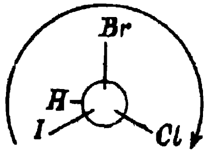


II

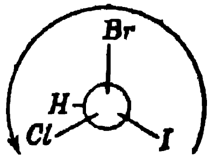
the sequence of priority is I, Br, Cl, H.

Step II. *The molecule is next visualised so oriented that the group of lowest priority is directed away from us, and arrangement of the remaining groups observed.* If in proceeding from the group of highest priority to the group of second priority and thence to the third, our eye travels in a clockwise direction, the configuration is termed **R** (Latin : *rectus*=right). If the eye travels in anticlockwise direction, the configuration is specified **S** (Latin : *sinister*=left).

Viewed in this manner the configurations **I** and **II** of bromochloroiodomethane given above are specified **R** and **S** respectively.



R



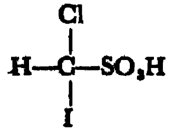
S

The racemic modification is specified by the prefix RS. For example, racemic lactic acid is written as (RS)-lactic acid.

It must, however, be clearly understood that unless we happen to know experimentally for a specific compound, (R)- or (S)- configuration gives no idea about the actual direction of optical rotation.

17. Sequence Rules.—Various sequence rules, which we shall need in our study, are given below :

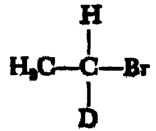
Rule 1. In case of four different atoms attached to the asymmetric carbon atom, priority depends on atomic number, with the atom of higher atomic number getting higher priority. If the two atoms are isotopes of the same element, atom of higher mass number has higher priority. For example, in chloroiodomethanesulphonic acid the sequence is I, Cl, S, H. Similarly, the sequence in α-deuterioethyl bromide is Br, C, D, H.



$$\mathrm{H{-}\overset{\displaystyle Cl}{\underset{\displaystyle I}{C}}{-}SO_3H}$$

Chloroiodomethanesulphonic acid

;



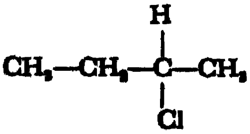
$$\mathrm{H_3C{-}\overset{\displaystyle H}{\underset{\displaystyle D}{C}}{-}Br}$$

α-Deuterioethyl bromide

______. Write the mirror ___ forms of both of these and using the sequence rule given above label each as ___ or S.

Rule 2. If two atoms attached to the chiral carbon atom are the same, rule 1 cannot decide the priority. In such cases compare the atoms attached to each of these first atoms.

For example, in *sec*-butyl chloride,

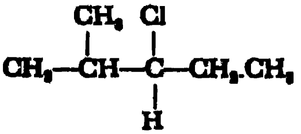


$$CH_3-CH_2-\underset{Cl}{\overset{H}{C}}-CH_3$$

the relative priority of CH_3 and C_2H_5 is decided as follows :

In CH_3, the second atoms are H, H, H ; in C_2H_5 they are C, H, H. Since carbon has a higher atomic number than hydrogen, C_2H_5 has the higher priority. Hence the sequence of priority is Cl, C_2H_5, CH_3, H.

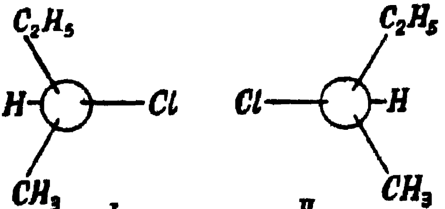
Similarly, in 3-chloro-2-methylpentane



$$CH_3-\overset{CH_3}{CH}-\underset{H}{\overset{Cl}{C}}-CH_2.CH_3$$

C, C, H of isopropyl takes priority over C, H, H of ethyl. Hence the complete sequence of priority is Cl, $(CH_3)_2CH$, C_2H_5, H.

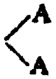
Exercise. *Label the following configurations I and II for sec-Butyl chloride as R and S.*

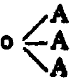


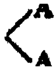
I II

[Ans. I is S and II is R.]

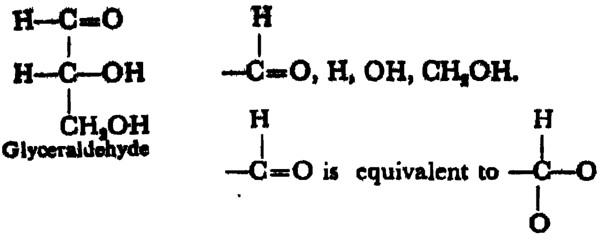
Rule 3. A doubly- or triply-bonded atom A is considered as equivalent to two or three A's respectively. For example,

=A is equivalent to  and

≡A is equivalent to 

(Real , however, has priority over =A.)

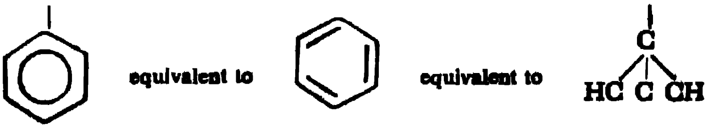
For instance, in glyceraldehyde the four groups attached to the chiral carbon atom are :


Glyceraldehyde

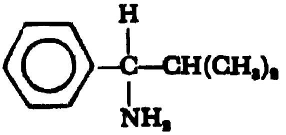
Out of these four groups, the OH group has the highest priority of all. Next O, O, H of —CHO takes priority over the O, H, H, of —CH$_2$OH. Thus complete sequence of priority is :

$$—OH, —CHO, —CH_2OH, —H$$

Phenyl group, C$_6$H$_5$— is considered as if it had only one Kekule structure :



Various groups attached to the chiral carbon atom in 2-methyl-1-phenylpropanamine,

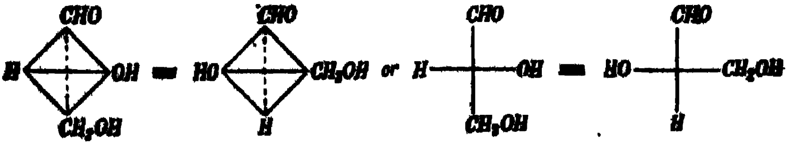


are : C$_6$H$_5$—, —NH$_2$, —CH(CH$_3$)$_2$, H.

Out of these, N of NH$_2$ has the highest priority. Next the C, C, C of phenyl takes priority over C, C, H of isopropyl. The entire sequence of priority is then NH$_2$, C$_6$H$_5$, C$_3$H$_7$, H.

Exercise. *Write the object and its mirror image configurations of* $C_6H_5CH(CH_3)NH_2$ *and label them as R and S.*

If any two groups attached to a chiral carbon atom are interchanged, the enantiomorph results. If a second interchange is made, the original form is regained. To designate the configuration of a chiral carbon atom, the necessary double interchange is made to place the group of lowest priority at the bottom of the perspective or projection formula as illustrated for (+)-glyceraldehyde.

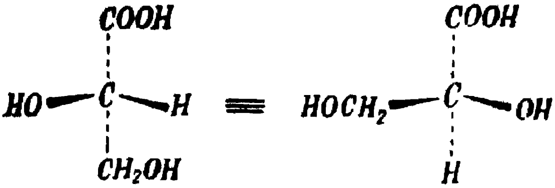


R-glyceraldehyde *R*-glyceraldehyde

(Fisher projections)

The sequence of priority being OH, CHO, CH_2OH, H, it has the *R* configuration.

Similarly, making necessary double interchange in (+) glyceric acid, we get



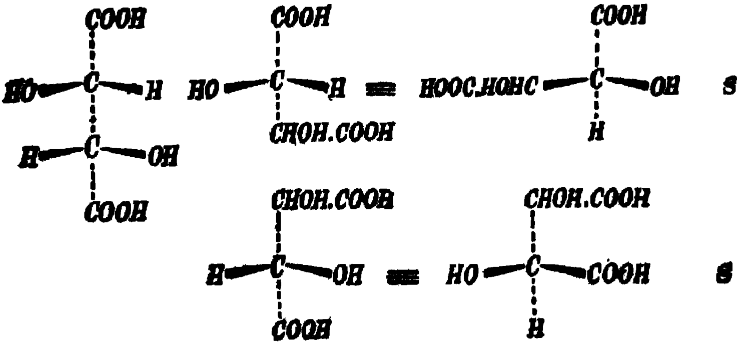
S-glyceric acid

(Prospective formnlae)

The sequence of priority being OH, COOH, CH_2OH, H, (+)-glyceric acid has *S*-configuration.

18. Specification of configuration of compounds with more than one chiral carbons.—Compounds like tartaric acid contain more than one chiral carbons. Specification of their configuration presents no special problem. We specify the configuration about each of the chiral carbons and with the help of numbers tell as to which configuration refers to which carbon.

For (−)-tartaric acid the sequence of groups attached to each chiral carbon atom is OH, COOH, CHOH.COOH, H. We specify the configuration about each of the two chiral carbon atoms by making necessary double interchange as follows :

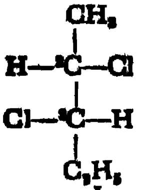


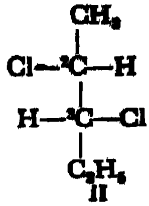
−)-Tartaric acid

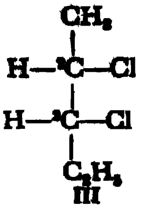
Hence (−)-tartaric acid is *S*, *S*-tartaric acid.

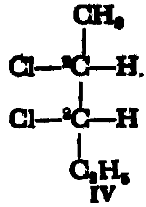
If a compound has two or more different chiral carbon atoms, the position of the chiral atom is indicated by a numeral preceding the configurational designation, as is demonstrated in the following examples.

In 2,3-dichloropentane the four configurations are given below :

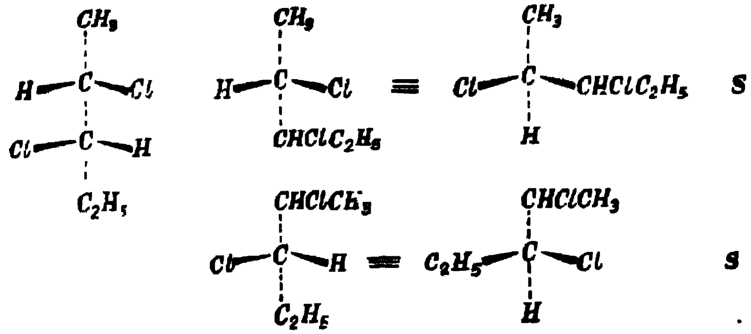

I


II


III


IV

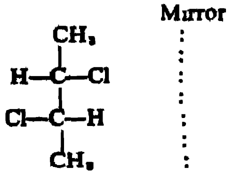
In the order of priority the four groups attached to C_2 are Cl, $CH_3.CH_2.CHCl$, CH_3, H. Those attached to C_3 are Cl, $CH_3.CHCl$, C_2H_5, H. Proceeding as before in the case of tartaric acid, we specify the configuration about each of the two chiral carbon atoms in **I**, by making necessary double interchange as follows :



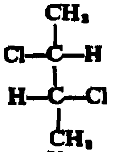
Thus we find that both C_2 and C_3 have S-configuration. Hence **I** has the configuration (2S, 3S) and it is named as (2S, 3S) -2, 3-dichloropentane.

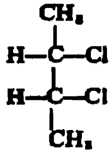
Similarly, **II** has the configuration (2R, 3R), **III** has the configuration (2S, 3R) and **IV** has configuration (2R, 3S).

Exercise. *Three stereo-isomers of 2, 3-dichlorobutane are given below. Specify their configuration in R and S notation.*



I


II


III

[**Ans.** I is (2S, 3S) ; II is (2R, 3R) ; III is (2S, 3R)]

19. Stereochemistry and Stereoisomerism.—Study of organic chemistry is based on molecular structure and properties. The branch of organic chemistry dealing with structure *in three dimensions* is termed **stereochemistry** (Gr. *stereos*=solid). An important aspect of stereochemistry is *stereoisomerism*. Isomers which differ from each other only in the way the atoms are oriented in space are called stereoisomers.

Optical isomers like that of lactic acid and tartaric acid are related as object and its mirror image. These mirror-image isomers are called *enantiomers*. **Enantiomers** *have identical physical properties except for the direction of rotation of the plane of polarised light. They have identical chemical properties except towards optically active reagents.* Since they differ from one another only in the way the atoms are oriented in space, enantiomers belong to the general class called stereoisomers. Stereoisomers that are not mirror images of each other are called **diastereoisomers.**

Thus according to the latest classification,

(*i*) Stereoisomers are of two distinct types : enantiomers and diastereoisomers.

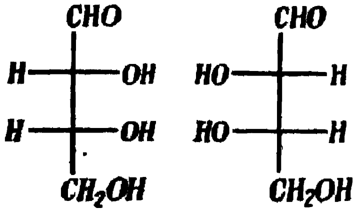
(*ii*) Enantiomers result from chirality only whereas diastereoisomers may result from chirality or from *cis-trans* isomerism.

(*iii*) Chiral system may be enantiomeric or diastereoisomeric whereas *cis-trans* isomers are always diastereoisomeric and never enantiomeric.

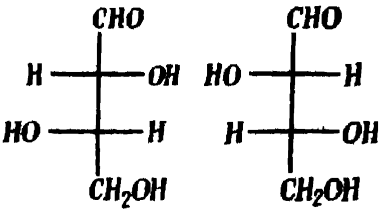
Sugars represented by the molecular formula,

$$CH_2OH\ .\ CHOH\ .\ CHOH\ .\ CHO$$

are erythrose and threose, each existing in two enantiomeric forms as given below :



(1) (2)
Two enantiomers of erythrose



(3) (4)
Two enantiomers of threose

Sugars represented by (1) and (3) are diastereoisomers not enantiomers.

29. Fischer Projections.—On pages 199 and 200 we have seen perspective formulae for glyceric acid and Fischer projections given for glyceraldehyde. In the perspective formulae thick horizontal lines represent bonds directed towards the reader and the dotted vertical lines represent bonds directed away from the reader.

In the Fischer projection

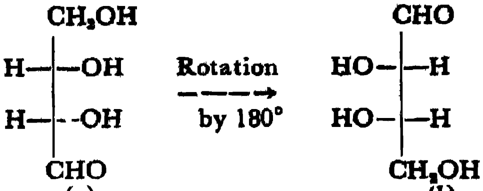
(1) The intersection of the horizontal and vertical lines represents the chiral centre (the chiral carbon atom).

(2) The horizontal lines represent bonds directed towards the reader.

(3) The vertical lines represent bonds directed away from the reader.

(4) Fischer projection formulae retain their configuration on rotation by 180° angle within the plane of the paper. Formula

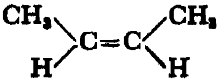
(*b*) given below is obtained on rotation of (*a*) by 180° within the plane of the paper. Hence (*a*) and (*b*) possess identical configurations.



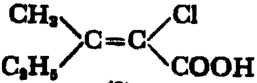
(*a*) (*b*)

21. The Prefixes threo- and erythro-.—Molecules with two different chiral centres, not necessarily on adjacent carbon atoms, are often designated by the prefix *threo-* or *erythro-*. The molecules with two identical (or similar) groups on the same side of the carbon chain in their Fischer projection formulae, are termed *erythro-*. On the other hand, molecules with two identical (or similar) groups on the opposite sides, are termed *threo-*.

22. More About Geometrical Isomerism—The (E, Z) System.—The terms *cis/trans* and *syn/anti* are being widely used to describe geometrical isomers in double-bond stereoisomerism. In a few cases, however, these terms are found to be inadequate in describing the isomers without ambiguity. For example, in the following compounds, (1) is obviously *cis* but (2) is not obviously *cis* or *trans*.



(1)



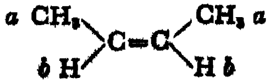
(2)

A new system of labels (E and Z) have been introduced to name such double-bond isomers unambiguously. These labels have been derived from the German words *entgegen* (meaning opposite) and *zusammen* (meaning together). The proposed system of nomenclature involves the following two steps :

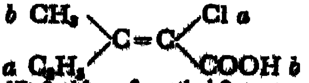
Step I. *Following the set of sequence rules given under R and S Notations on page* 197, *a sequence of priority* (*a and b*) *is assigned to the two groups at one end of the double bond. Similarly, a sequence of priority* (*a and b again*) *is assigned independently to the two groups at the other end of the double bond.*

Step II. *The configuration in which the two a groups are on the same side is labelled* (*Z*) *and another in which the two a groups are on opposite sides, is labelled* (*E*).

Following these two steps of priority assignments and labelling the configuration, the names of the compounds (1) and (2) are :

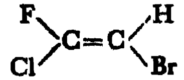


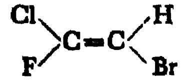
(*Z*)-2-butene

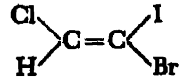


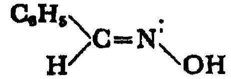
(*E*)-2-chloro-3-methyl-2-pentenoic dacid

Example 1. ***Give the E-Z designation of each of the following :***

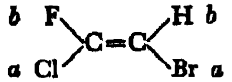
(*i*)


(*ii*)


(*iii*)


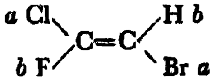
(*iv*)


On priority assignment and labelling, the E-Z designations of various compounds given above are :

(*i*)


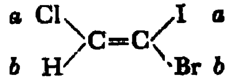
Z

(*Two a groups are on the same side*)

(*ii*)


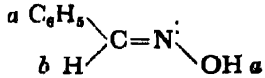
E

(*Two a groups are on the opposite sides*)

(*iii*)


Z

(*Two a groups are on the same side*)

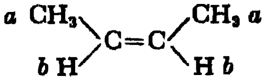
(*iv*)


E

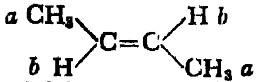
(*Two a groups are on the opposite sides*)

Note. When no atom is present in a position, as in (*iv*) above, consider the position to have an atomic number zero, *i.e.*, priority (*b*).

All those compounds which can be designated *cis* without ambiguity are designated ***Z***. Similarly, all those compounds that we would normally designate *trans* are designated *E*. For example,

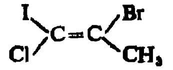


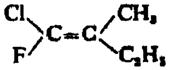
(*Z*)-2-Butene (*cis*-2-butene)

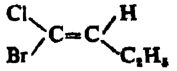


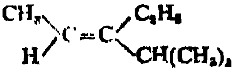
(*E*)-2-Butene (*trans*-2-butene)

Exercise. Give the *E-Z* designation of each of the following :

(*a*)


(*b*)


(*c*)


(*d*)


Ans. (*a*) Z (*b*) E (*c*) Z (*d*) E

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23. Resolution.—Whenever an optically active compound is synthesised in the laboratory the dextro and the laevo varieties are obtained in equal amounts and a racemic mixture results. The two components called enantiomorphs can, however, be obtained from the racemic mixture. ***The separation of a racemic mixture into its enantiomorphs (dextro and laevo components) is termed* Resolution.**

Due to identical physical properties of the optical isomers, their separation cannot be effected by simple methods like fractional crystallization or fractional distillation. Following methods have been used for resolving racemic compounds :

(1) **Mechanical Separation**. When the two isomers [(+)- and (−)-*varieties*] or their salts form well-defined crystals showing hemihedral faces, they can be separated by simple hand picking. Pasteur (1848) separated in this manner crystals of sodium ammonium racemate, $Na.NH_4.C_4H_4O_6.2H_2O$.

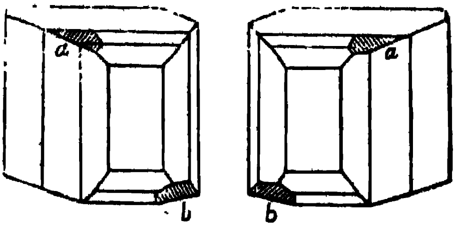


Fig 11·26—Crystals of sodium ammonium racemate showing hemihedral faces.

It should be noted that below a certain temperature, the isomers crystallize separately while they crystallize above this temperature as the racemic variety. This temperature is also influenced by the nature of the solvent. This method though simple in principle always offers some experimental difficulties resulting in its limited application. It is, therefore, mainly of historical interest at present.

(2) **Biochemical Separation** (Pasteur, 1858). This method is based on the fact that certain lower organisms, such as moulds, bacteria or fungi when allowed to grow in a solution of the racemic compounds destroy one of the optical isomers at a much quicker rate than the other due to *selective assimilation.*

For example, when *Penicillium glaucum* (a species of green mould) is allowed to grow in a solution of ammonium racemate, it destroys the (+)-tartrate by assimilation leaving behind the (−)-tartrate practically unaffected.

Though slow, the method is of wide application. The separation, however, is not always complete and one component is always lost. Some other side-products may also be formed and the sample may be difficult to purify.

(3) **By means of Salt-formation** (Pasteur, 1858). This method is the best of all methods of resolution. It consists in converting the active constituents of a racemic mixture into diastereoisomers (salts) with another active base or acid.

$$(\text{D}_{\text{acid}} + \text{L}_{\text{acid}} + 2\text{D}_{\text{base}} \longrightarrow (\text{D}_{\text{acid}}\ \text{D}_{\text{base}}) + (\text{L}_{\text{acid}}\ \text{D}_{\text{base}})$$

Racemic mixture (acid) — Active base — Optically active salts (*Diastereoisomers*)

The two salts thus obtained often differ in their solubilities and can be separated by fractional crystallization. The salts can be hydrolysed with inorganic acid or alkalis to get the original active compounds.

For example, salts of racemic acid [(±)-tartaric acid with (+)-cinchonine are (+)-cinchonine (+)-tartrate and (+)-cinchonine (−)-tartrate. On crystallization from a saturated solution, the latter being less soluble crystallizes out first. *Dextro* and *laevo* varieties of tartaric acid can be prepared by hydrolysis of these salts.

Bases used for the purpose are mainly alkaloids, *e.g.*, quinine, brucine, cinchonine and morphine. Similarly, acids commonly used for resolution are tartaric acid and camphorsulphonic acid.

(4) **Selective Adsorption.** Optically active substances may be selectively adsorbed by certain optically active adsorbents. For example, Henderson and Rule (1939) separated the active constituents of racemic camphor using dextro-lactose as an adsorbent.

24. **Racemisation.**—When a solution of (+)-tartaric acid in water is heated, it is transformed into a completely inactive mixture of the *racemic* and *meso*-tartaric acid. *The phenomenon of spontaneous production of the laevo variety from the dextro variety and* vice versa *to produce racemic mixture is called Racemisation.*

If a molecule of an optically active compound contains two or more chiral carbon atoms and the configuration of only one of these carbon atoms changes in a certain reaction, the process is termed **Epimerisation.**

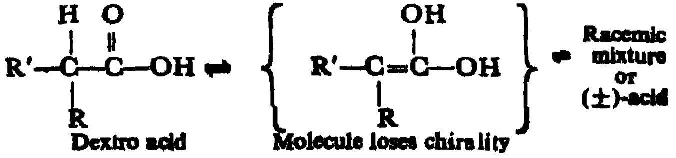
Racemisation can be brought about by :

(*i*) **The action of heat.** A rise in temperature always favours racemisation. Lactic acid, amyl alcohol, tartaric acid, etc., give racemic mixture on heating.

(*ii*) **Treatment with chemical reagents.** Presence of foreign substances favours racemisation in many instances. Many substances undergo racemisation when treated with chemical reagents, *e.g.*, mandelic acid ($C_6H_5CHOHCOOH$) with hydrobromic acid forms the corresponding (±)-bromo-acid.

(*iii*) **Autoracemisation.** In some cases racemisation occurs spontaneously at room temperature, *e.g.*, dimethyl bromosuccinate isomerises on standing at room temperature. This type of racemisation is termed *autoracemisation.*

Mechanism of Racemisation. One important set of compounds which readily racemise are those in which the chiral carbon atom is joined to a hydrogen atom and negative group. This readily undergoes tautomeric change and racemisation occurs *via* enolisation. For example,



$$R'-\underset{R}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-OH \rightleftharpoons \left\{ R'-\underset{R}{C}=\overset{OH}{C}-OH \right\} \rightleftharpoons \text{Racemic mixture or } (\pm)\text{-acid}$$

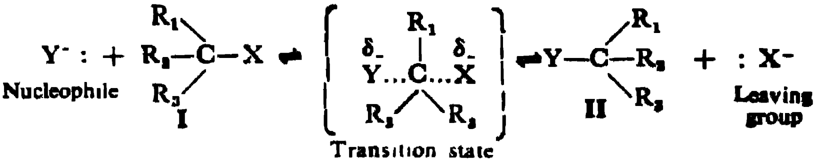
When the intermediate enol form, which is not chiral, reverts to the stable form, there are equal chances to produce the dextro and laevo forms. So it gives a racemic mixture.

In case of some other compounds which cannot undergo tautomeric change, *e.g.*, limonene, the mechanism of racemisation is uncertain.

25. **Walden Inversion.**—When an alkyl halide is attacked by a nucleophile (Y) from the back side, there is substitution of the leaving group (X) by the nucleophile. Since two species are taking part in this substitution reaction, it is termed bimolecular substitution by the nucleophile or S_N2 reaction.

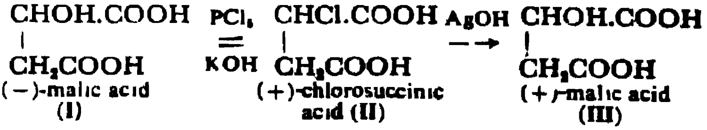
As the nucleophile approaches the carbon atom, the bond C—X is stretched. At a certain stage both Y and X are partially bonded to the carbon atom, *i.e.*, bond C—X is not yet completely broken and the bond Y—C is not yet completely formed. This state of the molecule is termed the *transition state*.

The transition state resembles an sp^2 hybridized carbon atom with three sp^2 orbitals lying in one plane, defined by the central carbon and its three substituents (R_1, R_2 and R_3). The Y—C—X axis lies perpendicular to this plane. As the leaving group X leaves and the bond Y—C is completely formed, the central atom undergoes a type of flipping, *i.e.*, the tetrahedron inverts just like an umbrella turning inside out in a windstorm. This type of inversion is termed a *Walden inversion*.



Walden inversion is easily detected if the central carbon happens to be a chiral carbon atom, *i.e.*, when R_1, R_2 and R_3 are different groups, since the optical activity of **I** is generally opposite to that of **II**.

Walden (1893, 1895) was able to convert an optically active compound (*laevo*-malic acid) into its enantiomer by a series of replacement reactions.



$$\begin{array}{c}\text{CHOH.COOH}\\ |\\ CH_2COOH\end{array} \underset{KOH}{\overset{PCl_5}{\rightleftharpoons}} \begin{array}{c}\text{CHCl.COOH}\\ |\\ CH_2COOH\end{array} \xrightarrow{AgOH} \begin{array}{c}\text{CHOH.COOH}\\ |\\ CH_2COOH\end{array}$$

(−)-malic acid (I) (+)-chlorosuccinic acid (II) (+)-malic acid (III)

The interchange of position between the two groups in the transformation of (−)-malic acid to (+)-malic acid has taken place in one and only one of the two steps given above. Thus if the configuration of (III) corresponds to that of (I), the inversion has taken place in the second step, *i.e.*, between (II) and (III). Any such change involving inversion of configuration is now termed *Walden Inversion*.

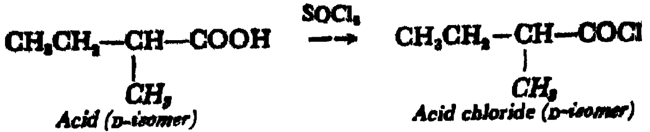
As it is, there is no way of telling in which step of the above experiment inversion has taken place. According to Kenyon (1925) inversion occurs only when the bond between the chiral carbon atom and another atom is ruptured. For example, esterification of an acid by an alcohol proceeds as follows :

$$RCO{-}OH\ H{-}OR' \longrightarrow RCO{-}OR' + H_2O$$

In this reaction since R′—O bond of the alcohol R′OH remains intact, no inversion is possible in alcohol.

In a number of chemical reactions a pure optical isomer yields the same pure isomer or another pure optical isomer as a result of Walden inversion. In all these reactions either the chiral centre remains unaffected or it is affected in a known predictable manner, *e.g.*, in S_N2 reactions. For example :

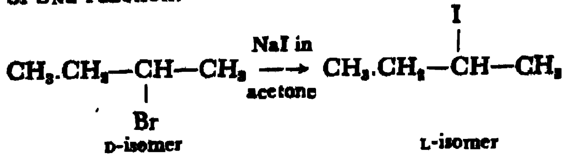
(*i*) An acid on reatment with thionyl chloride changes into acid chloride with no change in configuration. This is because the chiral centre remains unaffected.



$$CH_3CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-COOH \xrightarrow{SOCl_2} CH_3CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-COCl$$

Acid (D-isomer) Acid chloride (D-isomer)

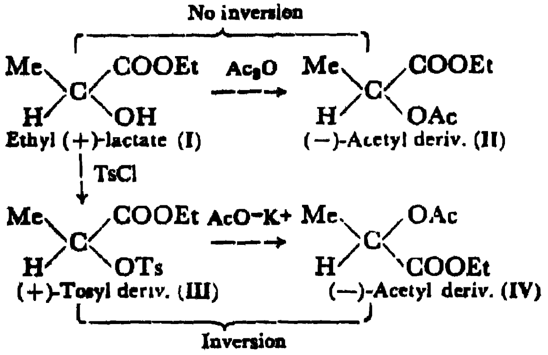
(*ii*) 2-Bromobutane on treatment with a solution of NaI in acetone changes into 2-iodobutane with a change in configuration as a result of S_N2 reaction.



$$CH_3.CH_2-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3 \xrightarrow[\text{acetone}]{\text{NaI in}} CH_3.CH_2-\overset{\displaystyle I}{\overset{|}{CH}}-CH_3$$

D-isomer L-isomer

Similarly, ethyl (+)-lactate can be converted into its acetyl derivative with or without change in configuration as given below :



Ethyl (+)-lactate (I) (−)-Acetyl deriv. (II)

(+)-Tosyl deriv. (III) (—)-Acetyl deriv. (IV)

Ts=tosyl group=*p*-toluenesulphonyl group *p*-$MeC_6H_4SO_2$.

In the above transformations (I) and (II) have the same relative configurations although (I) is dextro-rotatory while (II) is laevo-rotatory, *i.e.*, the sign of rotation has changed.

Conversion of (I) into tosyl derivative involves neither change in sign of rotation, nor change in configuration. However, treatment of tosyl derivative with potassium acetate (AcO^-K^+) produces (IV) which is an enantiomer of (II). This suggests that conversion of (III) into (IV) involves inversion whereas (II) and (III) are produced from (I) without inversion. This is accounted for by the fact that in the formation of (II) or (III) the C—O bond in (I) is never broken. However, during the conversion of (III) into (IV) the complete OTs group is replaced by OAc group, *i.e.*, C—O bond is broken and this results in inversion.

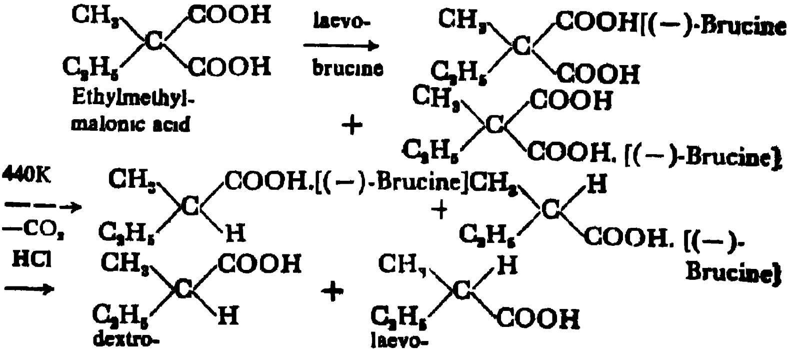
From this we learn that if inversion takes place in a displacement reaction at all, the complete group attached to the chiral centre must be removed. Its converse, however, is not true, *i.e.*, removal of a complete group attached to the chiral centre during a displacement reaction does not always result in inversion. For example, Kenyon showed that conversion of (+)2-octanol into (+)-2- Bromooctane does not involve any change in configuration.

26. **Asymmetric Synthesis.**—Whenever an optically active compound is synthesised in the laboratory, the product is always a racemic mixture which has to be resolved *to get optically active constituents. It is, however, possible to prepare an optically active isomer in the laboratory using special means without the necessity of resolution.*

The production of an optically active compound from a symmetric molecule without recourse to resolution is termed asymmetric synthesis.

Various methods used for asymmetric synthesis are :

(1) **With optically active reagents.** The first asymmetric synthesis was that of laevo-isovaleric acid carried out by Marckwald (1904) by heating the half brucine salt of ethylmethylmalonic acid at 440K.



The laevo-variety was in excess to the extent of about 10%.

Mackenzie (1905) reduced pyruvic esters in which alcohol was optically active (*e.g.*, laevo- manthol, laevo-amyl alcohol). The lactic ester produced gave on hydrolysis slightly laevo-rotatory lactic acid.

$$CH_3.CO.COOR+2[H] \xrightarrow{Al/Hg} \underset{\text{Lactic ester}}{CH_3.CHOH.COOR}$$

$$\xrightarrow{H_2O} \underset{\substack{\text{Lactic acid}\\ (\textit{slightly laevo-rotatory})}}{CH_3.CHOH.COOH}$$

(2) **With enzymes.** (−)-Mandelic acid has also been synthesised by treating benzaldehyde with hydrocyanic acid in the presence of the enzyme *emulsin* (present in almonds) with subsequent hydrolysis.

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO}+HCN \longrightarrow \underset{\text{Mandelonitrile}}{C_6H_5CH(OH)CN} \xrightarrow{H_2O} \underset{\text{Mandelic acid}}{C_6H_5CH(OH).COOH}$$

The (−)-variety is obtained in large excess of the (+)-isomer. Enzymes are complex and probably optically active organic compounds and possibly play the same role as an optically active substance in (1).

In nature a number of optically active compounds are being produced in the bodies of animals and plants probably under the influence of enzymes.

(3) **With circularly polarized light.** Many attempts have been made to produce optically active compounds by carrying on their synthesis under the influence of circularly polarized light. This is a special case of asymmetric synthesis and is known as *absolute asymmetric synthesis*. The first conclusive evidence for this was obtained by Kuthu and Knopf (1930). Some effect has been noticed but the method is not yet an experimental success.

TEST YOUR UNDERSTANDING

1. Pair each of the terms : (*a*) composition, (*b*) constitution, and (*c*) configuration with the proper counterpart among the terms (*i*) structural formula, (*ii*) space formula, and (*iii*) molecular formula.

2. Pair each of the terms : (*a*) optical activity, (*b*) double refraction, (*c*) enantiomers, and (*d*) resolution, with (*i*) separation into enantiomers, (*ii*) calcite, (*iii*) rotation of the plane-polarised light, and (*iv*) optical isomers.

3. Predict the number and kind of stereoisomers (active, meso or geometric) theoretically possible for each of the following compounds :

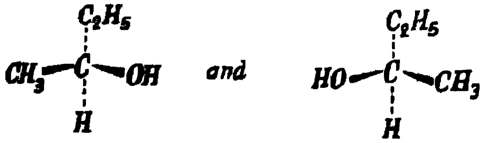
(*a*) $(CH_3)_2\,CH.CH\,(NH_2)\,COOH$, (*b*) $C_2H_5.CH\,(CH_3)\,CH_2OH$,

(*c*) $CH_3.CHBr.\,CH_2.CHBr.CH_3$, (*d*) $CH_2OH.(CHOH)_4.CHO$.

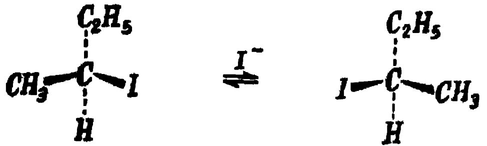
4. Pair each of the following terms with the appropriate examples : (*a*) geometric isomerism, (*b*) enolization, (*c*) enantiomorphism, (*d*) racemization, (*e*) asymmetric synthesis, (*f*) diastereoisomer, and (*g*) *meso* forms :

(*i*) $CH_3CH_2CH_2CHO \rightleftharpoons CH_3CH_2CH{=}CHOH$

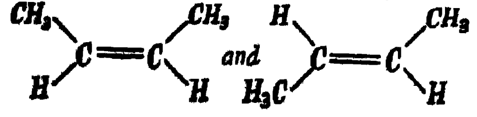
(*ii*)

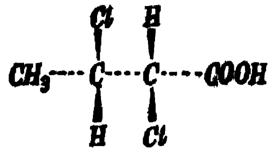
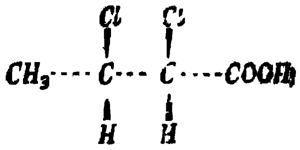


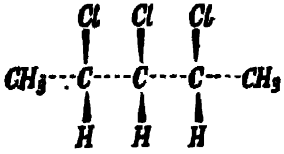
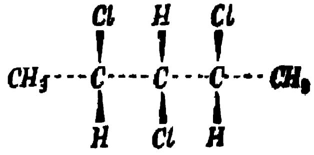
(*iii*)



(*iv*)

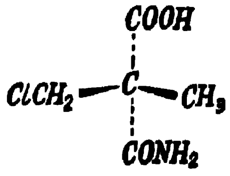


(v)  and 

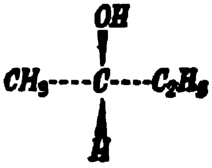
*(vi)  and 

(vii) $CH_3COCOOH \xrightarrow{\text{REDUCTASE OF YEAST}}$ (−) LACTIC ACID

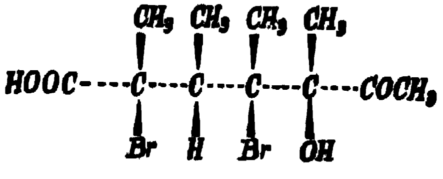
5. Specify as *R* or *S* the configuration of each chiral carbon atom in the following compounds :



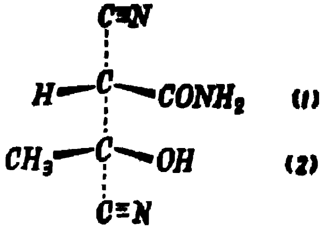
(a)



(b)



(c)



(d)

6. Compare the dextrorotatory and laevorotatory forms of 2-butanol $CH_3.CH_2CHOH.CH_3$, with respect to :

(*a*) b.p. ; (*b*) m.p. ; (*c*) sp. gravity ;
(*d*) specific rotation ; (*e*) refractive index ; (*f*) solubility ;
(*g*) rate of reaction with HBr ; (*h*) specification as *R* or *S*.

7. Which of the following objects are chiral :

(*a*) nail, screw, pair of scissors, knife,

(*b*) glove, shoe, sock, pullover sweater, coat sweater,

(*c*) basket ball, football, tennis racket, shotgun barrel, rifle barrel, and

(*d*) your hand, your foot, your ear, your nose, yourself.

KEY

1. (*a*)—(*iii*) ; (*b*)—(*i*) ; (*c*)—(*ii*).
2. (*a*)—(*iii*) ; (*b*)—(*ii*) ; (*c*)—(*iv*) ; (*d*)—(*i*).
3. (*a*), (*b*)—two active ; (*c*)—two active and one meso ; (*d*)—sixteen active.
4. (*a*)—(*iv*); (*b*)—(*i*) ; (*c*)—(*iii*) ; (*d*)—(*iii*) ; (*e*)—(*vii*) ; (*f*)—(*v*) (*g*)—(*vi*).
5. (*a*) *S* ; (*b*) *S* ; (*c*) *1S*, *2S*, *3R*, *4R*, (*d*) *1R*, *2S*.
6. Equal but opposite specific rotation ; opposite R/S specification ; all other properties the same.
7. (*a*) screw, pair of scissors. (*c*) football (laced), rifle barrel.
   (*b*) glove, shoe, coat sweater. (*d*) all.

QUESTIONS

Essay Type :

1. What do you understand by the term 'optical activity' ? Explain it with special reference to tartaric and lactic acids. (*Rajasthan B.Sc. 1971*)

2. (*a*) "Optical activity of a molecule is linked with the presence of chiral carbon atom or atoms in it." Justify.

(*b*) Write a brief explanatory note on relation between chirality and optical activity.

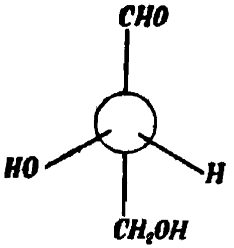
3. Give an account of isomerism exhibited by lactic acid. What is meant by resolution ? Describe at least two methods for resolving a racemic mixture. (*Punjab B.Sc. 1971*)

4. Write an essay on specification of configuration using the *R* and *S* notation.

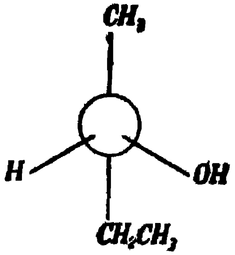
5. (*a*) What are Diastereoisomers ? Bring out the differences between and Diastereoisomers.

(*b*) Explain what you understand by Rectus and Sinister system of of chiral centres ?

(*c*) IUPAC names have been assigned to the following compounds. the configuration about each chiral centre according to the Rectus-Sinister system by placing *R* or *S* in the parenthesis provided.



(2)-2, 3-Dihydroxypropanal



(2)-2-Butanol

(*Guru Nanak Dev B.Sc. 1971*)

6. Give an account of the theoretical basis of optical and geometrical isomerism with special reference to (*a*) Lactic acid, (*b*) Tartaric acid and isomers having the formula $C_4H_4O_4$ and $C_4H_6O_5$. (*Rajasthan B.Sc. 1970*)

7. Discuss Le Bell and van't Hoff theory of optical isomerism with special reference to tartaric acid. How is meso tartaric acid prepared ? (*Jabalpur B.Sc. 1973*)

8. What is tautomerism ? Give examples. Discuss the structure of one such compound. How does resonance differ from tautomerism ? (*Nagpur B.Sc. 1973*)

9. Write the appropriate formula corresponding to each name in the following pairs and mention the type of isomerism exhibited by each pair :

(*i*) anti-*n*-butane and gauche-*n*-butane.

(*ii*) vinyl alcohol and actaldehyde.

(*iii*) L-lactic acid and D-lactic acid.

(*iv*) acetone and propionaldehyde.

(*v*) *o*-dichlorobenzene and *p*-dichlorobenzene.

(*vi*) *n*-butane and isobutane. (*Osmania B.Sc. 1975*)

10. What are geometric isomerism and optical isomerism ? Give examples. Why is fumaric acid not optically active ? (*Utkal B.Sc. 1976*)

11. Give an account of the isomerism of maleic and fumaric acids. How are the isomers identified ? How is one isomer converted into the other ? (*Madras B.Sc. 1976*)

12. Write a detailed note on : Optical isomerism in tartaric acids. (*Andhra B.Sc. 1976*)

13. Write the names and appropriate formulae of one pair of example for each of the following :

(*a*) Functional isomers, (*b*) Diastereoisomers, (*c*) Conformers. (*Andhra B.Sc. 1976*)

14. Describe any one method of resolving a racemic mixture of

(*a*) Tartaric acid. (*Bangalore B.Sc. 1978*)

(*b*) Lactic acid. (*Delhi B.Sc. Hons. 1978*)

15. Explain what is meant by Walden inversion. (*Calicut B.Sc. 1978*)

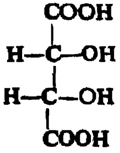
16. Outline two methods of resolution of racemates. (*Calicut B.Sc. 1978*)

17. Explain the following with examples :

(*a*) Chain isomerism and (*b*) Geometrical isomerism. (*Calicut B.Sc. 1978*)

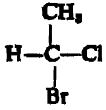
18. Label the following compounds with *R* and *S* notations :

(*i*)



$$\begin{array}{c} COOH \\ | \\ H-C-OH \\ | \\ H-C-OH \\ | \\ COOH \end{array}$$

(*ii*)



$$\begin{array}{c} CH_3 \\ | \\ H-C-Cl \\ | \\ Br \end{array}$$

(*Delhi B.Sc. Hons. 1978*)

19. What are the elements of symmetry. Explain giving one example of each. (*Delhi B.Sc. Hons. 1978*)

20. What do you understand by conformation ? How would you explain the greater stability of chair form of cyclohexane as compared to that of boat form ? (*Delhi B.Sc. Hons. 1978*)

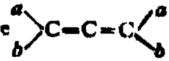
Short Answer Type :

1. Write briefly conformations of *n*-butane. (*Andhra B.Sc. 1974*)

2. In how many stereoisomers can HOOC—CHOH—CHOH—COOH exist ? (*Andhra B.Sc. 1974*)

3. Lactic acid exhibits optical isomerism whereas propionic acid does not. Explain why. (*Andhra B.Sc. 1974*)

4. Explain why *cis*-1, 3-dimethylcyclohexane is more stable than its trans-isomer. (*Andhra B.Sc. 1974*)

5. Account for the fact that compounds of the type  can be resolved into optical isomers. (*Calicut B.Sc. 1972*)

6. Write briefly on keto-enol tautomerism. (*Kerala B.Sc. 1975 ; Madras 1974 ; Andhra 1973*)

7. What type of isomerism does lactic acid exhibit ? (*Kerala B.Sc. 1973*)

8. How does resonance differ from tautomerism ? (*Nagpur B.Sc. 1973*)

9. Write a short note on Geometric Isomerism. (*Nagpur B.Sc. 1973 ; Bangalore 1974 Supp.*)

10. Write a short note on : Isomerism of tartaric acid. (*Nagpur B.Sc. 1973 ; Sri Venkateshwara 1972 ; Bangalore 1974*)

11. Write a short note on : isomerism of organic compounds. (*Ravi Shankar B.Sc. 1974 ; Bangalore 1974*)

12. How will you differentiate between Asymmetry and chirality ? (*Delhi B.Sc. Hons. 1977*)

13. How will you differentiate between Enantiomers and diastereoisomers ? (*Delhi B.Sc. Hons. 1977*)

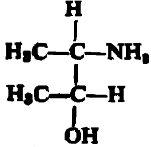
14. Differentiate between configuration and conformation. (*Delhi B.Sc. Hons. 1977*)

15. How will you differentiate between *cis-trans* and *syn-anti* forms of geometrical isomers ? (*Delhi B.Sc. Hons. 1977*)

16. What is the difference between racemic and meso forms ? (*Delhi B.Sc. Hons. 1977*)

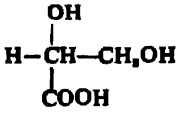
17. Give the absolute configuration at each of the chiral carbon atoms in the following two compounds :

(*i*)



$$\begin{array}{l} \qquad\;\; H \\ \qquad\;\; | \\ H_3C-C-NH_2 \\ \qquad\;\; | \\ H_3C-C-H \\ \qquad\;\; | \\ \qquad\;\; OH \end{array}$$

and (*ii*)



$$\begin{array}{l} \qquad\;\; OH \\ \qquad\;\; | \\ H-CH-CH_2OH \\ \qquad\;\; | \\ \qquad\;\; COOH \end{array}$$

(*Delhi B.Sc. Hons. 1977*)

18. Different conformers of dichloroethane cannot be isolated. Explain, why. (*Delhi B.Sc. Hons. 1977*)

19. Explain the term 'Polarized light (*G.N.D. B.Sc. 1977*)

20. What is the requirement for a compound showing optical activity ? (*G.N.D. B.Sc. 1977*)

21. Write a short note on optical activity. (*G.N.D. B.Sc. 1977*)

22. Give two examples of optically active compounds. (*G.N.D. B.Sc 1973*)

23. Define the following with suitable examples :

(*i*) Diastereoisomerism. (*ii*) Optical isomerism.
(*iii*) Racemate. (*iv*) Meso form. (*Calicut B.Sc. 1975*)

24. Illustrate with suitable examples · Enantiomers, diastereoisomers, epimers and meso compounds. (*Burdwan B.Sc. Hons. 1971*)

25. Write a note on conformational analysis. (*Andhra B.Sc. 1975*)

26. Write a note on optical isomerism. (*Andhra B.Sc. 1973 ; Bangalore 1973 ; Calicut 1974*)

27. Write a short note on Chain and Position Isomerism. (*Madras B.Sc. 1977*)

28. Write a short note on Walden Inversion. (*Madras B.Sc. 1976, 74 ; Calicut 1972*)

29. Write a short note on Asymmetric Synthesis. (*Madras B.Sc. 1976, 74*)

30. Mention the specific type of isomerism exhibited by each of the following pairs :

(*a*) 1, 2-Dibromoethane and 1, 1-dibromoethane.
(*b*) Vinyl alcohol and acetaldehyde.
(*c*) *n*-Butyl alcohol and diethyl ether. (*Andhra B.Sc. 1978*)

31. Write short but critical note on :

(*a*) Anomers. (*Andhra B.Sc. 1978*)
(*b*) Keto-enol tautomerism. (*Andhra B.Sc. 1977*)

32. Which of the following alkenes exhibits *cis-trans* isomerism ? Write the structures of the isomers :

(*a*) 1-Butene, (*b*) 2-Butene, (*c*) Isobutene. (*Andhra B.Sc. 1977*)

33. Write structures of the stereo-isomers possible in each of the following :

(*a*) $H_3C-CHCl-CHCl-CH_3$.
(*b*) $H_3C-CHBr-CBr_2-CH_3$. (*Andhra B.Sc. 1977*)

34. What is meant by :

(*i*) Dihedral angle, (*ii*) Gauche conformation,

(*iii*) *Anti* conformation, (*iv*) *Syn* conformation. (*Andhra B.Sc. 1977, 76*)

35. Write briefly on : Absolute configuration of a molecule. (*Andhra B.Sc. 1976*)

36. Write the possible stereoisomers for each of the following :

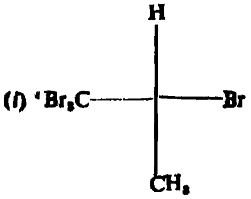
(*a*) CH_3—CH(OH)—CH(OH)—CH_3.

(*b*) HO_2C—CH(CH_3)—CH(Cl)—CO_2H (*Andhra B.Sc. 1976*)

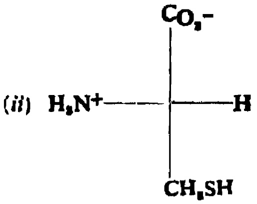
37. Write the Newman projection formulae of the conformations possible for butane. Which one of them is the preferred conformation ? (*Andhra B.Sc. 1976*)

38. Give the configuration *R* or *S* at each of the asymmetric carbon atoms in the following compounds :

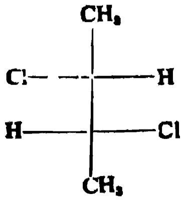
(*i*)



(*ii*)



(*iii*)



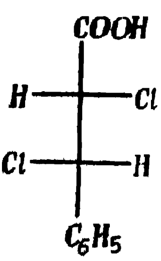
(*Delhi B.Sc. Hons. 1979*)

39. Furmaric acid and maleic acid give the same anhydride on heating but fumaric acid must be heated to a much higher temperature than maleic acid to effect the same change. Explain. (*Delhi B.Sc. Hons. 1979*)

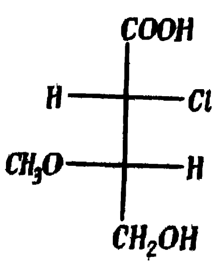
40. What do you understand by configuration and conformation ? Explain the difference by taking suitable examples. (*Delhi B.Sc. Hons. 1979*)

41. What do you understand by erythro- and threo- prefixes ?

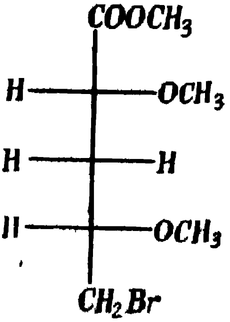
42. *Which of the following Fischer projections represent the erythro- molecules and which ones the threo- molecules ?*



(1)



(2)



(3)

[Ans. (1) *threo-* (2) *threo-* (3) *erythro-*]

12

Spectroscopy

1. **Introduction**—Determination of constitution of a newly discovered compound was a major problem and took years. It involved breaking of molecules into fragments, study the composition of each fragment, and then finding how these were linked in the original molecule.

Since the 1940s there has been a revolution in this field and the problem is now tackled by spectroscopic methods. Structures of even complicated molecules are established in a few days. Advantages of spectroscopic methods over the other known techniques are :

(*i*) These are very quick and extremely sensitive.

(*ii*) Information obtained is in the form of a permanent record and is highly reliable.

(*iii*) Very small quantity (only a few milligrams) of the substance are required for the determination and even this quantity can be recovered at the end of the experiment.

2. **Origin of Electronic Spectra.**—Different types of electronic spectra are :

(*a*) **Emission Spectra.** When a substance is subjected to intense heat or to an electric discharge, its atoms or molecules absorb energy and get excited. These excited species, on returning to the ground state, may emit radiation which on passing through a prism gives rise to a spectrum. This type of spectrum is termed emission spectrum. When recorded on a photographic plate, emission spectrum of atoms appears as bright lines on a dark background, whereas that of molecules appears as bands.

(*b*) **Absorption Spectra.** When white light is passed through a prism, we get a continuous spectrum of seven colours and sodium light gives a line spectra —two D-lines (yellow) of definite wavelength. These are both examples of emission spectra.

When white light is passed through sodium flame before reaching the prism, we get a continuous spectrum with two black lines in place of yellow lines obtained from sodium light. Here sodium flame has absorbed two wavelengths from white light which it itself emits. This is an example of an obsorption spectrum. Let us understand the principle underlying such absorption.

During absorption some of the molecules in the path of incident beam collide with photons of radiant energy. However, only those photons get absorbed whose energy exactly equals the difference in energy, ΔE between the ground and excited states of the molecules.

$$\Delta E = h\nu = hc/\lambda$$

or energy absorbed per mole $= N_A hc/\lambda$

wherein h (Planck's constant) $= 6{\cdot}63 \times 10^{-34}$ Js

c (velocity of electromagnetic radiation) $= 3 \times 10^{8}$ ms^{-1}

$$N_A = 6{\cdot}02 \times 10^{23} \text{ mol}^{-1}$$

∴ Energy absorbed per mole

$$= \frac{(6{\cdot}02 \times 10^{23})(3{\cdot}0 \times 10^{8} \text{ms}^{-1})(6{\cdot}63 \times 10^{-34} \text{ Js})}{\lambda(\text{nm}) \times 10^{-9} \text{m per nm}}$$

$$= \frac{2{\cdot}86 \times 4{\cdot}18 \times 10^{7}}{\lambda(\text{nm})} \text{J}$$

If $\lambda = 286$nm,

$$\text{energy} = 4{\cdot}18 \times 10^{5} \text{ J mol}^{-1} = 100 \text{ kcal mol}^{-1}$$

(sufficient to bring about many chemical reactions).

Organic compounds cannot exist under drastic conditions necessary to stimulate these for giving emission spectra. They give rise to only absorption spectra.

Types of Absorption Spectra. The internal energy of a molecule may be regarded as the sum of electronic, vibrational and rotational energies.

$$E_{int} = E_{elec} + E_{vib} + E_{rot}$$

(*a*) **Ultraviolet Spectroscopy.** For each electronic level within the molecule, energy separation is about 100 kcal mol^{-1}. Electronic excitation, therefore, requires energetic photons of $\lambda \sim 286$nm from UV region (200 – 400 nm). This is UV spectroscopy.

(*b*) **Infra-red Spectroscopy.** Between two successive electronic levels A and B, there are a number of associated vibrational levels, the energy separation between them being a tenth to a hundredth of that between A and B. Further each vibrational level is itself associated with a set of rotational states with energy separation of the order of a hundredth of that between two vibrational levels.

Photons from IR region (2000 – 20,000nm) have sufficient energy to excite the molecule from one vibrational level to another. In IR spectroscopy radiation absorbed causes *stretching and bending* of organic bonds.

(*c*) **Nuclear Magnetic Resonance (NMR) Spectra.** NMR spectra represents the wavelengths of radiations absorbed by atomic nuclei in strong magnetic fields.

Another type of spectra we come across are **Mass Spectra.** However, these are not spectra at all, according to our definition of spectra, since these are only records of masses of particles produced when atoms or molecules are bombarded by beams of electrons with very high energies.

3. **Laws of light absorbance.**—Electronic spectra of organic substances are most frequently recorded in solution and the Beer-Lambart law (Eqn. 1) expresses mathematically the relationship between the amount of light absorbed and (*a*) the concentration of the solution and (*b*) the length of the solution through which light passes.

$$\log_{10} \frac{I_0}{I} = \varepsilon c l \ldots\ldots(1)$$

or $A = \varepsilon \times cl$ or $\varepsilon = A/cl$

wherein I_0 = intensity of incident light

I = intensity of transmitted light

c = concentration of absorbing compound in moles per litre.

l = length of sample tube in cm

ε (epsilon) is called absorptivity or molecular extinction coefficient. A is termed absorbance of the solution

$$A = \log \frac{I_0}{I} = \log \frac{1}{I} \quad \text{or} \quad I = \frac{I}{I_0}$$

I is termed transmittance of solution.

The wavelength at which a molecule has its highest absorption coefficient (ε_{max}), is designated λ_{max}. A spectrum may have several different maxima each with its characteristic value of ε_{max}.

Problems 1. A 2×10^{-5} M solution of an organic compound, X placed in a 1 cm tube has an absorbance (A) of 0·63 at $\lambda_{max} = 237$ nm. Calculate the value of ε_{max} for X.

Hint. $\varepsilon_{max} = A/lc = 0{\cdot}63/1 \times (2 \times 10^{-5}) = 31{,}500$

2. A solution of the same compound X placed in a 10 cm tube has an absorbance (A) = 0·21 at $\lambda_{max} = 237$nm. Calculate the concentration of the solution.

Hint. $\varepsilon_{max} = A/lc$

or $$c = \frac{A}{\varepsilon_{max} \times l} = \frac{0{\cdot}21}{10 \times 31500} = 6{\cdot}67 \times 10^{-7}\text{M}$$

[$\varepsilon_{max} = 31{,}500$ as calculated in (1) above]

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4. **Presentation of Spectral data.**—The absorption spectrum of an organic compound is usually represented as a graph of absorbance, or absorptivity (ε or $\log \varepsilon$) against wavelength expressed in nm. For the sake of brevity for each absorption band only ε_{max} and λ_{max} are reported. Where molecular weight is unknown, ε

cannot be calculated. In such case $E_{1cm}^{1\%}$, *i.e.*, log (I_0/I) for 1% solution of 1 cm path length is plotted against wavelength.

Absorption maxima and *absorption minima* are those points on the absorption curve at which absorbance reaches a maximum or minimum respectively. An inflexion arises when a discontinuity or a shoulder appears upon a curve of increasing or decreasing absorbance.

Instrument used for measuring the amount of light absorbed at each wavelength of the incident radiation are termed **spectrometers** A record of the radiation absorbed by a given sample as a function of the wavelength of the incident radiation is termed absorption spectrum.

A *spectrograph* makes a photographic record of the spectrum and a *spectrophotometer* uses a photoelectric cell to provide a quantitative measure of the light intensity at each wavelength.

A spectrometer consists of a light source, a sample holder, a wavelength discriminator (or monochromator) and a recording device.

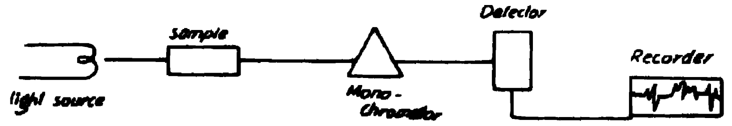

Fig. 12·1—Schematic diagram of a spectrometer.

ULTRAVIOLET SPECTROSCOPY

5. **Ultraviolet Spectroscopy.**—When an electromagnetic radiation in ultraviolet region (λ=200-400 nm) or visible region (λ=400-800 nm) is made to pass through a compound containing multiple bonds, it is observed that a part of the incident radiation is usually absorbed. The amount of radiation actually absorbed depends on the structure of the compound as well as the wavelength of the radiation. The energy of the radiation beam absorbed is used for excitation of electrons in orbitals of lower energy into orbitals of higher energy. Amount of light absorbed at each wavelength of ultraviolet or visible region is measured with the help of a spectrometer.

Modern spectrometers consist of a radiation source consisting of a tungsten lamp for producing visible light and a deuterium discharge lamp for producing ultraviolet radiations. These radiations are passed through a monochromator which automatically selects the required wavelengths. The monochromatic beam is split into two parallel beams one of which passes through a transparent cell containing very dilute solution of the organic compound. It is termed the sample beam. The second beam is directed through an identical cell containing solvent only. This is termed the reference beam. The intensities of the two transmitted beams are electronically compared and a plot of absorbance against wavelength is automatically recorded over the desired range.

Suppose the sample absorbs light at one particular wavelength, intensity of the sample beam emerging out of the sample (I_S) will be less than that of the reference beam (I_R). There is an automatic electronic device to plot a graph between wavelength and absorbance* (A) of light. The graph obtained is termed an *absorption* spectrum. One such spectrum is shown in Fig. 12·2. This

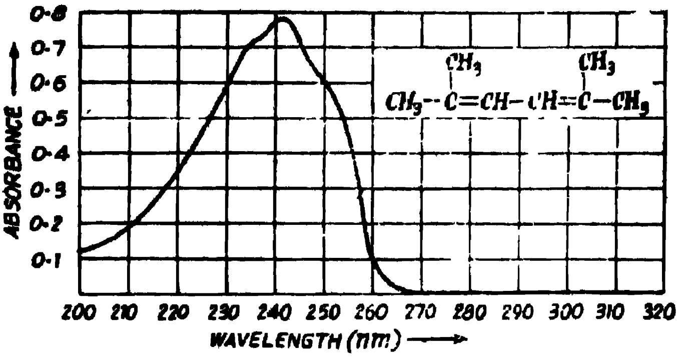

Fig. 12·2—UV absorption spectrum for 2, 5-dimethyl- 2, 4-hexadiene.

is UV absorption of 2,5-dimethyl-2,4-hexadiene. It show a broad absorption band in the region 210-260 nm with a maximum at 241·5 nm. It is this wavelength of maximum absorption (λ_{max}) which is reported in chemical literature.

Cell Construction, Range of Measurement and Solvents. Since glass cells contain impurities which absorb ultraviolet radiations, silica cells are used. Most spectrometers operate over a range of 190-750 nm*, *i.e.*, visible (400—750nm) and part of UV (labelled Near-UV in the electromagnetic spectrum shown in Fig. 12·3.

Cosmic and X-rays	Far UV	Near UV	Visible	Near IR	IR	micro wave

λ in nm	100	200	400	800	2000	20,000
Energy (kcal mol^{-1})	286	143	72	36	14	1·4
$\bar{\nu}$ (cm^{-1}) = $10^7/\lambda$ (nm)	100, 100	50,000	25,000	12,500	5000	500
ν (Hz) = $\bar{\nu} \times (3 \times 10^{10})$	3×10^{15}	$1·5 \times 10^{15}$	$7·5 \times 10^{14}$	$3·8 \times 10^{14}$	$1·5 \times 10^{14}$	$1·5 \times 10^{13}$

Fig. 12·3—The electromagnetic spectrum.

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* An older word for nanometer (nm) is *millimicron*, represented by the symbol mμ. Another unit used for measuring wavelengths is the *angstrom* unit symbolised as Å. 1 nm = 10 Å. Angstrom is being gradually replaced by nanometers.

The lower limit of 190 nm is set due to silica being increasingly less transparent at about this wavelength and constituents of air (particularly oxygen) begin to absorb strongly. Special vacuum techniques are needed for measurement below 190 nm.

Solvents used should be sufficiently transparent over desired range of wavelength. 95% ethanol is commonly used. It is transparent down to about 205 nm. Cyclohexane transparent down to 195 nm may be used in more detailed studies. In general polar compounds are more sensitive to change in solvent than non-polar ones.

6. **Electronic Energy Transitions.**—The absorption of ultraviolet and visible light by organic compounds invariably involves valency electrons (the only exception being organo-metallic compounds in which inner shell transitions of the metal atoms occur). These electrons may be forming single bonds (σ, sigma electrons), multiple bonds (π electrons), unshared electron pairs (n-electrons in case of elements of first two rows of the Periodic Table) or unpaired odd electrons (present in free radicals) and electrons in charged ions. A sigma (σ) electron is held tightly and a good deal of energy is required to excite it, that is outside the range of usual spectrometer. It is chiefly the excitation of the comparatively loosely held n and π electrons that appear in the ultraviolet spectrum. The modes of electronic energy changes which occur when radiation in ultraviolet and visible region is absorbed by an organic compound are summarised below :

(*a*) *Transition between bonding orbitals and anti-bonding orbitals* ($\sigma \rightarrow \sigma^*$), *i.e.*, bonding sigma to anti-bonding sigma or bonding pi to anti-bonding pi ($\pi \rightarrow \pi^*$)

(*b*) *Promotion of non-bonding electrons* (unshared pair, n) into anti-bonding sigma ($n \rightarrow \sigma^*$) or anti-bonding pi ($n \rightarrow \pi^*$). These involve transitions of non-bonding lone pair on a hetero atom (*e.g.*, O or N) to an empty non-bonding molecular orbital.

The electronic transitions of maximum concern to the organic chemist are (*a*) $n \rightarrow \pi^*$ in which the electrons of an unshared pair go to an unstable (anti-bonding) π^* orbital (*b*) $\pi \rightarrow \pi^*$, in which an electron goes from a stable (bonding) π orbital to unstable (antibonding) π^* orbital

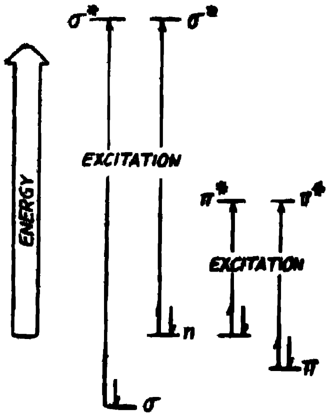
These possible transmissions are summarised in the following diagram (Fig. 12·4).

The general characteristics of $n \rightarrow \pi^*$ bands are low intensity (normally less than 1500) and are shifted to shorter wavelengths by more polar solvents as well as by electron donating groups. In the spectra of simple molecules $n \rightarrow \pi^*$ transitions require the least energy and the corresponding bands are of longest wavelength. The $\pi \rightarrow \pi^*$ bands are of shorter wavelength and $\sigma \rightarrow \sigma^*$ bands appear in the far-ultraviolet.

Simple chromophores consisting of multiple bonded units, such as,

$>C{=}C<$, $-C{\equiv}C-$, $-C{\equiv}N$, $-N{=}N-$, $>C{=}O$

undergo π—π^* transitions in short wavelength regions of ultraviolet. (Chromophores are units of structures which absorb selective wavelengths and even small structural changes bring about perceptible changes in the wavelength of the radiation absorbed.)



—Antibonding sigma (σ^*)

—Antibonding pi (π^*)

—Nonbonding *n* (*p*)

—Bonding π

—Bonding σ

Summary of Electronic energy levels

Fig. 12·4—Energies required for various electronic transitions

The absorption spectrum of a simple aliphatic ketone. *e.g.*, acetone, shows three absorption bands at $\lambda_{max} = \sim 160$, 190 and 280 nm. The short-wavelength band ($\lambda_{max} = 160$ nm) is due to an $n \rightarrow \sigma^*$ transition whereas the remaining two bands $\lambda_{max} = 190$ nm and $\lambda_{max} = 280$ nm given in cyclohexane solution are due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively. The $n \rightarrow \pi^*$ transition involves the non-bonded electrons of the oxygen atom of the carbonyl group. Energies of these principal orbitals are shown in Fig. 12·5.

7. **What Type of Compounds give UV Spectrum.**—All electrons in alkanes are lightly held in C—C or C—H σ bonds and need very high energy radiation for excitation ($\lambda_{max} = 135$ nm in far UV region) and cannot, therefore, be detected by UV spectrometers. Alkanes are transparent in near UV region and often used as solvents for UV spectra of other molecules.

Electrons in π bonds are much easier to excite than are σ electrons but unconjugated alkenes still absorb in the far UV region at 170—180 nm. In contrast the molecules with conjugated double bonds have strong absorption in the near-UV region.

This shift to absorption of longer wavelengths (lower energy) is due to the fact that excitation of electron from an orbital in a conjugated double bond leaves the remaining electrons free to spread out over all the *p*-orbitals. *Since the excited state is stabi-*

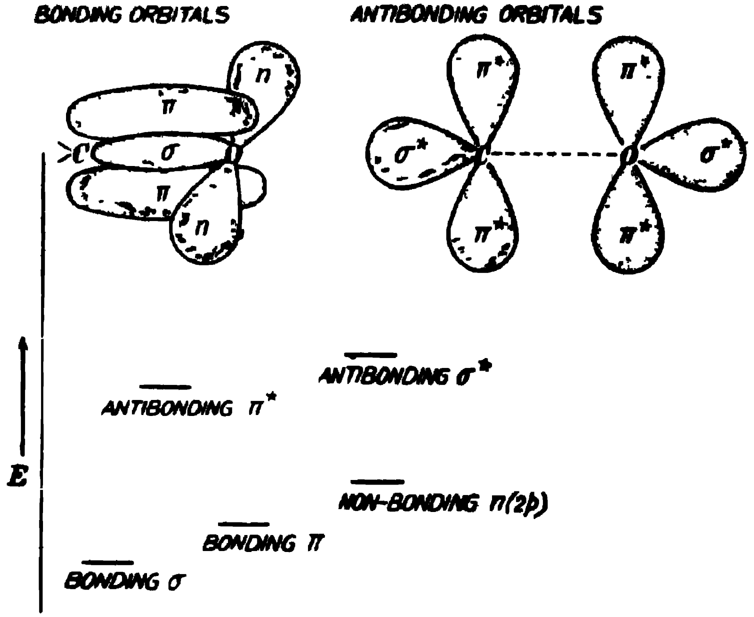
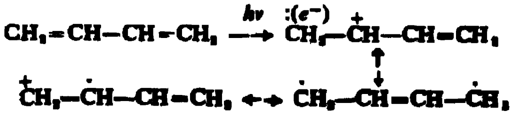


Fig. 12.5—Schematic representation of the principal orbitals (σ, σ*, n, π, π*) of the carbonyl group in simple aldehydes and ketones.

lised by resonance, it is easier to form than the excited state from an unconjugated double bond.

Problem. *Draw all the resonance structures for the excited state from photo-excitation of 1, 3-butadiene.*

[**Hint.**



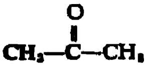
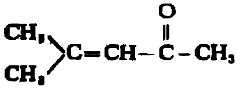
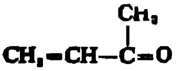
$$CH_2{=}CH{-}CH{=}CH_2 \xrightarrow{h\nu} \overset{:(e^-)}{C}H_2{-}\overset{+}{C}H{-}CH{=}CH_2$$
$$\updownarrow$$
$$\overset{+}{C}H_2{-}\dot{C}H{-}CH{=}CH_2 \leftrightarrow \dot{C}H_2{-}CH{=}CH{-}\dot{C}H_2$$

Write three more such canonical forms.]

When more than two double bonds are in conjugation, it is easier to move an electron into an upper energy level and even longer wavelengths will supply the needed energy. λ_{max} for polyenes with 7 or 8 such double bonds lies in the visible region. Even those with five conjugated double bond chains are often coloured yellow.

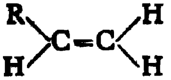
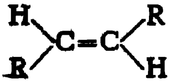
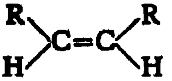
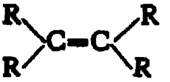
λ_{max} for some compounds having conjugated double bonds are given below for studying the trends of changes.

Table 12·1—UV spectra of conjugated molecules

Compound	λ_{max}
$CH_3-(CH=CH)_2-CH_3$	227
$CH_3-(CH=CH)_3-CH_3$	274
$CH_3-(CH=CH)_4-CH_3$	311
$CH_3-(CH=CH)_5-CH_3$	342
$CH_3-(CH=CH)_6-CH_3$	380
 $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$	270
 $(CH_3)_2C=CH-\overset{\overset{O}{\|}}{C}-CH_3$	237
 $CH_2=CH-\overset{\overset{CH_3}{\|}}{C}=O$	$n\rightarrow\pi^*$ $\lambda_{max}=324$ nm (very weak) $\pi\rightarrow\pi^*$ $\lambda_{max}=219$ nm

From the table given above, we find that λ_{max} increases with number of conjugated double bonds.

Further it increases with the alkyl substituents on the double bonds, as shown by the examples given below :

Alkene	*Approximate Absorption maxima*	
	monosubstituted	177 nm
	*trans*- di ,,	183 nm
	*cis* ,, ,,	180 nm
	Tetra ,,	200 nm

(R-*Alkyl group*)

Spectra of *cis*- and *trans*-disubstituted olefins show small but discernible differences on the basis of which we can distinguish between the two isomers.

Conjugated carbonyl compounds also absorb UV light. (Why ?) This is since π bonds of C=O groups replace C=C π bonds. Aromatic molecules and molecules with unsaturated heterocyclic rings also absorb near-UV light and often show several different maxima in their spectra.

Absorption with $\epsilon_{max} > 10^4$ is termed high intensity absorption and that with $\epsilon_{max} < 10^3$ is low intensity absorption. Transitions of low probability are forbidden transitions.

Summary of Electronic Structure and Transitions

Electron	*Example*	*Electronic transition*	λ_{max}	ϵ_{max}
σ	Ethane	$\sigma \rightarrow \sigma^*$	135	
n	Water	$n \rightarrow \sigma^*$	167	7000
π	Ethylene	$\pi \rightarrow \pi^*$	165	10,000
π and n	Acetone	$\pi \rightarrow \pi^*$	~150	—
		$n \rightarrow \sigma^*$	188	1,860
		$n \rightarrow \pi^*$	279	15
π—π	1,3-Butadiene	$\pi \rightarrow \pi^*$	217	21,000
Arom π	Benzene	Arom $\pi \rightarrow \pi^*$	~180	60,000
		,,	~200	8,000
		,,	253	215

Problem Write the structures of an organic compound that can undergo $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition by UV radiation. (*Osmania B.Sc. 1980*)

8. Some Other Factors which influene λ_{max}.

(*a*) **Effect of strain.** Compounds with conjugated double bonds absorb at higher wavelengths Maximum overlap of the π-orbitals and consequently most effective conjugation is possible only when σ-bond systems of the interacting unsaturated groups are coplanar. Factors which tend to diminish effective conjugation, raise the energy required for $\pi \rightarrow \pi^*$ transitions. This is why dienes whose structures exhibit ring strain or molecular overcrowding behave anomalously, and absorption occurs at shorter wavelengths. This will be illustrated by λ_{max} values of substituted nitrobenzene,

Compound	λ_{max}	ϵ
Nitrobenzene	252 nm	8,620
o Nitrotoluene	250 nm	5,950
o-Nitrocume	247 nm	3,760

The presence of increasingly bulky *ortho* substituents hinders the coplanarity which the nitro group achieves with the benzene ring. This results in shifting λ_{max} towards shorter wavelength.

In a pair of *cis* and *trans* isomers, the latter is expected to achieve coplanarity of π electron system more readily and show absorption due to $\pi \rightarrow \pi^*$ transition at longer wavelength than the *cis* isomer. For example,

Compound	*cis*-Isomers		*trans*-Isomer	
	λ_{max}	ϵ_{max}	λ_{max}	ϵ_{max}
Cinnamic acid	268	10,700	272	15,900
Stilbene	278	9,350	294	24,000

Strain decreases as we pass from cyclopentane to cyclohexane ring. As shown by the following compounds λ_{max} increases as the strain decreases.

(*i*) 2-cyclopentanone λ_{max} = 217 nm

2-cyclohexanone λ_{max} = 227 nm

(*ii*) 1-Acetylcyclopentene λ_{max} = 242 nm

1-Acetylcyclohexene λ_{max} = 237 nm (*b*) **Effect of Salt formation.**

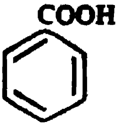
(*i*) **In phenol.** λ_{max} for phenol is 210·5 nm. Electron transfer is facilitated in the anion (C_6H_5O) and λ_{max} increases to 235 nm.

$$\underset{\lambda_{max}\ 210\cdot5\ \text{nm}}{C_6H_5OH} \longrightarrow \underset{235\ \text{nm}}{C_6H_5O^-}$$

(*ii*) **In Aniline.** Aniline absorbs at λ_{max}=230 nm due to $n \to \pi^*$ transition In the case of anilinium ion the unshared electron pair is no longer available for electron transfer (E.T.) transition, and the spectrum reverts to a toluene type and λ_{max} decreases to 203 nm.

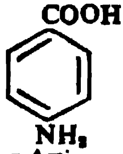
$$\underset{\lambda_{max}\ 230\ \text{nm}}{C_6H_5\ddot{N}H_2} \longrightarrow \underset{203\ \text{nm}}{C_6H_5\overset{+}{N}H_3Cl^-}$$

(*iii*) **In *p*-Aminobenzoic acid.** *p*-Aminobenzoic acid absorbs at 284 nm. In alkaline solution, the anion facilitates electron transfer. However, the cation present in strong acid solution absorbs at 226·5 nm (*cf.* λ_{max} for benzoic acid=230 nm). This is because the lone pair of the amino group is no longer available in the cation for $n \to \pi^*$ transition.



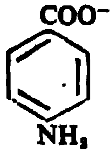
Benzoic acid

λ_{max} 230 nm



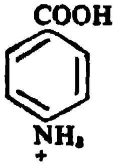
p-Aminobenzoic acid

284 nm



Anion

265 nm



cation

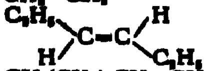
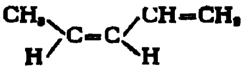
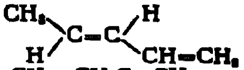
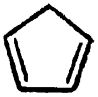
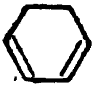
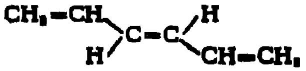
226 5 nm

(*c*) **Effect of Extended Conjugation.** In a conjugated double bond system the excitation of electron from an orbital leaves the remaining electrons free to spread over all the *p*-orbitals and the excited state is stabilised by resonance.

As a result of extended conjugation, the π electron system gets lengthened resulting in greater delocalization of the π electrons. As a result, the energy required for the $\pi \to \pi^*$ transitions is less and the probability of these transitions is higher. Extended conjugation, therefore results in a shift of the position of absorption by the system to longer wavelengths. For example λ_{max} for $CH_3-(CH=CH)_n-CHO$ is 217 nm when $n=1$, it is 270 nm when $n=2$ and 312 nm when $n=3$.

(*d*) **Effect of Hydrogen bonding.** Since hydrogen bonding stabilizes the excited state, electron transfer is facilitated resulting in a shift of the position of absorption by the system to longer wavelengths. For example, hydrogen bonding is possible in the case of *o*-nitrophenol, salicylic acid and salicylaldehyde. For each λ_{max} is greater than that of the corresponding *m* and *p*-derivatives.

Table 12·1—Longest Wavelength Absorption Maxima of some Unsaturated Hydrocarbons

Compound	*Structure*	λ_{max} (*nm*)	ϵ_{max}
Ethene	$CH_2{=}CH_2$	171	15,530
trans-3-Hexene	 $C_2H_5(H)C{=}C(H)C_2H_5$	184	10,000
1-Octene	$CH_3(CH_2)_5CH{=}CH_2$	177	12,600
Cyclohexene		182	7,600
Propyne	$CH_3{-}C{\equiv}CH$	187	450
1-Octyne	$CH_3(CH_2)_5\ C{\equiv}CH$	185	2,000
1, 3-Butadiene	$CH_2{=}CH.CH{=}CH_2$	217	21,000
cis-1, 3-Pentadiene	 $CH_3(H)C{=}C(H)CH{=}CH_2$	223	22,600
trans-1, 3-Pentadiene	 $CH_3(H)C{=}C(H)CH{=}CH_2$	223·5	23,000
1-Buten-3-yne	$CH_2{=}CH.C{\equiv}CH$	228	7,800
1, 3-Cyclopentadiene		239	3,400
1, 3-Cyclohexadiene		256	8,000
trans-1, 3, 5-Hexatriene	 $CH_2{=}CH(H)C{=}C(H)CH{=}CH_2$	274	50,000

9. Applications of Ultraviolet Spectroscopy.—Ultraviolet spectroscopy is not very helpful in the detection of individual functional groups. It is, however, useful in predicting the relationship between different groups especially with respect to conjugation existing between (*i*) two or more carbon-carbon multiple (double or triple) bonds, (*ii*) carbon-carbon and carbon-oxygen double bonds or (*iii*) carbon-carbon double bonds and aromatic ring.

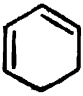
Example 12·1. *Two isomeric compounds X and Y have the molecular formula C_6H_8; Both of them decolorise bromine solution in CCl_4 as well as alkaline $KMnO_4$. Both of them give cyclohexane (C_6H_{12}) on catalytic hydrogenation. X shows an absorption maximum at 256 nm while Y shows no absorption maximum beyond 200 nm. What are the structures of X and Y?*

Solution :

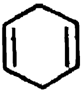
Both X and Y add four hydrogen atoms on catalytic hydrogenation to yield cyclohexane (C_6H_{12}). This shows both X and Y are cyclic hydrocarbons with two double bonds, *i.e.*, each one is a cyclohexadiene.

This inference is supported by its reactions : (*i*) decolorisation of Br_2 dissolved in CCl_4, and (*ii*) decolorisation of alkaline $KMnO_4$.

Their absorption maxima are 256 nm and <200 nm. From this we can infer that X with higher value of λ_{max} (=256) is a conjugated diene whereas Y with lower value of λ_{max} is not conjugated. Hence X is 1, 3-cyclohexadiene,



and Y is 1, 4-cyclohexadiene,



Example 12·2. *Three isomeric compounds* X, Y *and* Z *with molecular formula* (C_5H_6) *absorb three moles of hydrogen on catalytic reduction to give n-pentane.*

Y *and* Z *give a white ppt when passed through ammoniacal silver nitrate but* X *does not react with it.*

X *and* Y *show an absorption maximum near 230 nm whereas* Z *gives no absorption maximum beyond 200 nm. Identify* X, Y *and* Z.

Solution.

(*i*) All the three absorb 3 moles of hydrogen to give *n*-pentane. From this we can infer that they are unsaturated open-chain hydrocarbons each containing one double bond and one triple bond.

(*ii*) Since Y and Z give a white ppt with ammoniacal $AgNO_3$, the triple bond is present at the end of the chain in each,

$$C{-}C{-}C{-}C{\equiv}C$$

(*iii*) Since X does not give a white ppt with ammoniacal $AgNO_3$, triple bond in it does not lie at the end of the chain,

$$C{-}C{-}C{\equiv}C{-}C$$

(*iv*) Since both X and Y show an absorption maximum (λ_{max}) near 230 nm while Z gives it at λ_{max} <200 nm, both X and Y have conjugated bonds.

(*v*) Now X has a conjugated system of multiple bonds and the triple bond is not near the end. Its structure should be

$$H_2C{=}CH{-}C{\equiv}C{-}CH_3$$

1-Penten-3-yne

(*vi*) Y has a conjugated system of multiple bonds and the triple bond is situated at one end. Its structure should be

$$CH_3{-}CH{=}CH{-}C{\equiv}CH$$

3-Penten-1-yne

(vii) In Z the multiple bonds are not conjugated and the triple bond is situated at one end. Its structure should be

$$CH_2{=}CH{-}CH_2{-}C{\equiv}CH$$

1-Penten-4-yne

Answer the following Questions

1. Which is the region of greatest interest to organic chemist for UV and IR spectra ? What is the cause of absorption in UV and IR regions ? (*Delhi B.Sc. Hons.* 1977)

2. Can ultraviolet spectral data be useful to distinguish the compounds in the following pairs ? Give reasons.

(*i*) ethylbenzene and styrene ;

(*ii*) $CH_2{=}CH{-}CH_2{-}CH{=}CH_2$ and $CH_3{-}CH{=}CH{-}CH{=}CH_2$ (*Delhi B.Sc. Hons.* 1973)

3. Arrange the following in the increasing order of their UV absorption maxima.

(*i*) Anthracene, (*ii*) Ethylene,

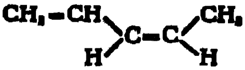
(*iii*) Naphthalene, (*iv*) Butadiene. (*Osmania B.Sc.* 197)

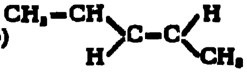
4. Compounds A, B and C have the formula C_5H_8 and on hydrogenation yield *n*-pentane. Their ultraviolet spectra show the following values of λ_{max} : A, 176 mμ : B, 211 mμ : C, 215 mμ (1-Pentene has λ_{max} 178 mμ).

(i) What are the likely structures for A, B and C ?

(ii) What kind of information might enable you to assign specified structures to B and C ? (*Punjab B.Sc.* 1976)

5. For the three dienes given below assign with justification the λ_{max} values from amongst 176 mμ, 211 mμ and 215 mμ.

(*a*) 

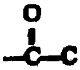
(*b*) 

(*c*) $CH_2{=}CH{-}CH_2{-}CH{=}CH_2$ (*Delhi B.Sc. Hons.* 1980)

6. (*a*) What are the advantages of using spectroscopic methods ?

(*b*) Give the principle of UV spectroscopy in brief.

(*c*) What wavelengths are absorbed by the following groups :

(*i*) $-C{=}C-$ (*ii*) $-C{=}C{-}C{=}C-$ (*iii*) 

$$-\overset{\overset{\displaystyle O}{\|}}{C}-C$$

(*d*) Why does a tomato appear red ? (*Guru Nanak Dev B.Sc.* 1982)

7. What type of compounds absorb UV radiations ? Select compounds in support of your answer from the following list :

(*i*) 1,3-butadiene, (*ii*) 1-hexene, (*iii*) cyclobutane, (*iv*) 1,3-cyclohexadiene, (*v*) chlorobenzene, (*vi*) nitrobenzene, (*vii*) chlorocyclohexane. (*Delhi B.Sc. Hons.* 1982)

Hints

2. (*i*) Extended conjugation in styrene resulting in bathochromic shift as compared to ethylbenzene.

(*ii*) Second is conjugated, hence this alone will give UV spectrum.

3. (*ii*)<(*iv*)<(*iii*)<(*i*)

4. A is 1, 4-pentadiene ; B is *cis*-1,3-pentadiene and C is *trans*-1, 3-pentadiene.

5. (*a*) 211 mμ (*b*) 215 mμ (*c*) 176 mμ

6. (*i*) 171 nm (*ii*) 227 nm (*iii*) 279 nm.

7. (*i*), (*iv*) and (*vi*)

INFRARED SPECTROSCOPY

10. Introduction.—*Radiations in the infrared (IR) region from about 800 to 20,000 nm are not energetic enough to cause electronic excitations in most organic molecules. IR radiations,* however, do cause stretching and bending of organic bonds. In all organic molcules bonds joining various atoms can stretch and bend and all of them absorb infrared radiation.

In contrast to the relatively few absorption peaks observed in the UV region for most organic compounds, the IR spectrum provides a rich array of absorption bands. Many of these bands cannot, however, be interpreted (assigned) accurately but those which can be assigned, provide a wealth of structural information about the molecule.

11. Range and Units employed. Wavelengths in IR region are usually measured in micrometres (μm) where 1 μm$=10^{-6}$m or 10^3 nm (fromerly called a *micron* represented by the symbol μ). IR region extends from about 0 8 to 20 μm and most of the commercial IR spectrometers cover the region from about 2 to 17 μm.

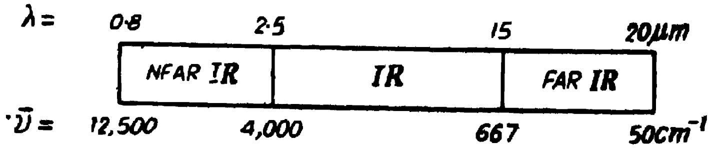


Fig 12'6—Range of IR spectrum

Ordinary IR region extends from 2'5 to 15 μm (4000 to 667cm^{-1}), The region extending from 0'8 to 2'5 μm (12500 to 4000 cm^{-1}) is called the *near infrared* region whereas the one extending from 15 to 200 μm (667 to 50 cm^{-1}) is termed the *far infrared* region.

IR spectra are, commonly described in terms of the frequencies of radiations absorbed rather than their wavelengths. This is logical since frequency is directly proportional to the energy of the radiation whereas wavelength is inversely proportional to energy. The most common unit used to describe IR spectra is the wave-number, $\bar{v}$ which represents the number of vibrations of radiation per centimetre (cm^{-1}). Wavelengths in μm can be converted into wave-numbers by the formula

$$\bar{v} = 10^4/\lambda \qquad [\because\ 1\mu m = 10^{-6}m = 10^{-4}\ cm$$

It is rather annoying that while in UV spectra we make use of λ in nm, for IR spectra the units employed are μm for wavelength(λ) and cm^{-1} for wave-number (ν). Workers in respective fields, are used to these units and it is difficult to persuade them to change for the sake of uniformity.

12. Molecular Vibrations and Origin of IR Spectrum.—A molecule is not a rigid assemblage of atoms It may be considered to resemble a system of balls of various masses corresponding to the atoms of a molecule and springs of varying strengths corresponding to the chemical bonds of a molecule. There are two kinds *of fundamental vibrations in the molecules :*

(*i*) ***Stretching*** *in which the distance between two atoms* decreases or increases.

(*ii*) **Bending or deformation** in which the position of the atoms changes relative to the orginal bond axis.

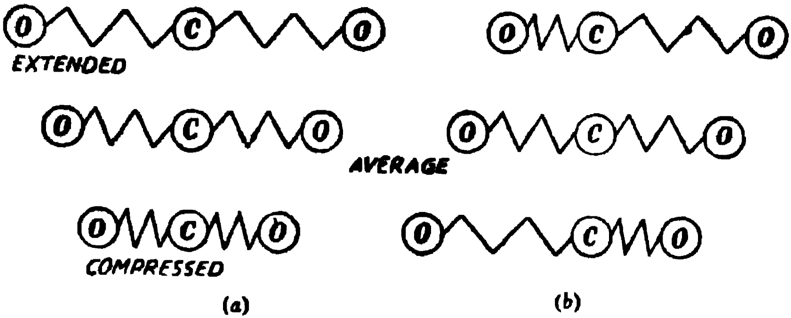
Various stretching and bending vibrations of a bond occur at certain quantized frequencies. When infrared light of the same frequency is incident on the molecule, energy is absorbed resulting in increase of amplitude of vibration. When the molecule reverts from the excited state to the original ground state, the absorbed energy is released as heat.

Thus absorption in the IR region implies the occurrence of vibrational transitions in a molecule while it remains in its ground electronic state.

A non-linear molecule that contains n atoms has $3n$ 6 possible fundamental vibration modes that can be responsible for the absorption of IR light. Regarding the molecule as a loose collection of atoms, each of which may have its movement resolved along three mutually perpendicular directions, we can see that the system has a total of $3n$ degrees of freedom Movement of whole molecule as a rigid unit will take up six of these degrees of freedom, three translational and three rotational (two rotational in the case of a linear molecule). So for vibratory motion, where the atoms move relative to each other, we are left with $3n$-6 ($3n-5$ for a linear molecule) degrees of freedom or fundamental vibrational modes. For CH_4 and C_6H_6,($3n-6$)=9 and 30 respectively.

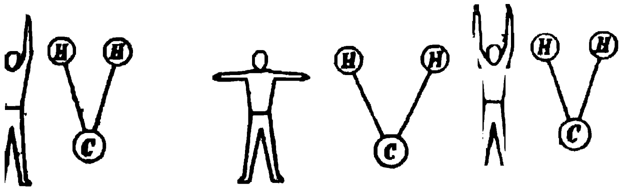
In order for a particular vibration to result in the absorption of infrared energy, **that vibration must cause a change in the dipole moment** *of the molecule.* The molecules that contain certain symmetry elements will display somewhat simplified spectra. For example C=C stretching vibrations of ethylene and symmetrical C—H stretching of the four C—H bonds of methane do not result in an absorption band in this IR region

Some of the various stretching vibration modes that are possible within a molecule are shown below for a typical triatomic molecule CO_2 (Fig. 12 7) Similarly various possible bending vibration modes for a typical triatomic group $>CH_2$ are depicted in Fig. 12·8.

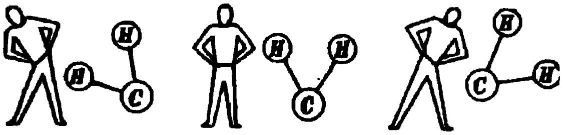


(a) (b)

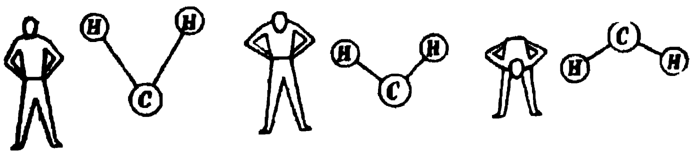
Fig. 12·7—Bond streching vibration modes for CO_2, a typical triatomic molecule (a) Symmetric, (b) Anti-symmetric.



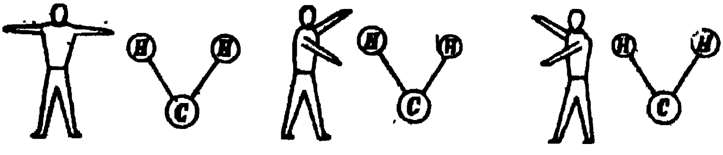
(a) *Scissoring* (In-plane deformation). The bond angle changes ; the carbon atom moves in and out.



(b) *Rocking* (In-plane deformation). The bond angle is constant.



(c) *Wagging* (Out-of-plane deformation). Both hydrogen atoms move simultaneously up and down out of the plane.



(d)—*Twisting* (Out-of-plane deformation). One hydrogen atom moves up while the other moves down out of the plane.

Fig. 12·8—Bending modes [(a) to (d)]. Molecules like CH_4 containing more than two atoms have bond angles which are continuously changing like under conditions of molecular vibration.

Bending vibrations generally require less energy and occur at longer wavelength **(lower wave number)** *than stretching vibrations.* **Stretching vibrations are found to occur in the order of bond strengths. For example**

C≡C	4·4—5·0 μm	(2300—2000 cm^{-1})
C=C	5·3—6·7 μm	(1900—1500 cm^{-1})
C–C, C–N & C—O	7·7—12·5 μm	(1300—800 cm^{-1})

When single bond involves very small proton (C—H, O—H or N—H) stretching vibrations occur at much higher frequency, 2·7—3·8 μm (3700—2630 cm^{-1})

O—H	2·8 μm (3570 cm^{-1}).
O—D	3·8 μm (2630 cm^{-1})

Absorption peaks caused by stretching vibrations are usually the most intense peaks in the spectrum. Some bond frequencies that interest the organic chemist are shown below :

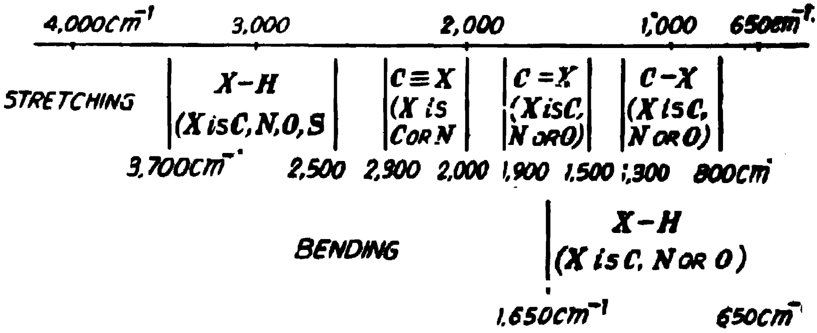


Fig. 12·9—Important bond frequencies that interest the organic chemist.

The complexity of most organic spectra is understandable when a molecule of 20 atoms would in theory have $(3n-6)$, *i.e.*, 54 fundamental vibrations. However there are the following two *saving features* :

(*a*) Since many of these atoms will be carbon and hydrogen, some of the vibrational frequencies will be coincident or degenerate.

(*b*) Furthermore, a structural group of the type AX_2 or AX_3 having two or more identical adjacent bonds, will vibrate as a unit with symmetrical and antisymmetrical modes of slightly different energies.

13. Instrumentation.

(*i*) **Light Source.** A common source of light for infrared radiation is the *Nernst glower*—a moulded rod containing a mix-

ture of zirconium oxide, yttrium oxide and erbium oxide that is heated to around 1500°C by electrical means.

(2) **Cells and Prisms.** Glass and quartz as well as metals absorb IR radiation. IR spectrum cannot, therefore, be recorded in glass or quartz cells. Prisms used in the construction of IR spectrometers (to separate IR beams into their component wavelengths) also cannot be made of glass. IR cells and prisms are, therefore, usually made of common salt (NaCl) which is transparent to most IR radiations. It is, however, not an ideal material for holding various solutions for IR studies since it is soluble in water and many alcohols. If damp solvents are used, they dissolve the cells gradually. It is also brittle and cracks easily.

(3) **Solvents.** Common solvents used for IR studies are CCl_4, CS_2 and $CHCl_3$ but each one of these absorbs a part of the IR spectrum.

(4) **Technique** : (*a*) **Use of Double Beam Spectrometer.** Solvent absorbs a part of the IR spectrum. This can be counteracted to some extent by using a double beam spectrometer. This splits the IR beam into two halves One half of these passes through the solvent cell containing only the solvent while the other half passes through a sample cell containing the solution under examination.

Each half of the beam then falls on a separate detector in the spectrometer. By proper adjustment the solvent absorptions in the two halves of the beam cancel each other out and thus absorptions recorded are characteristic of the solute only.

Most modern spectrometers are of double beam type. The technique, however, is not completely satisfactory since solvents might absorb all the radiations at some wavelengths. Spectra is, therefore, taken using different solvents (*e g.*, CCl_4 and CS_2) which are transparent in different IR regions. These are combined to obtain a complete spectrum.

(*b*) **Using Potassium bromide.** Another technique is to avoid the use of solvents altogether. This works well with liquids which can be studied in thin films.

Solids which are insoluble in CCl_4 or CS_2 are ground into fine powder and pressed into pellets with potassium bromide which is essentially transparent to IR radiation in the 2—17 μm region. Pressed powder pellets may, however, disperse much of IR radiation and give poor spectra.

Dispersion may be partially decreased by making a paste of the solid powder in mineral oil or polymerised fluoroalkanes. These mateials, however, block out part of the spectrum.

14. Applications of IR Spectroscopy

(*a*) **Detection of Functional Groups.** In a given environment, a certain functional group will absorb IR energy of very nearly the same wavelength in all molecules. For example, acetone and dihexyl ketone give absorption peaks at the same place. It is, however, different from that for acetic acid (on account of electrical effect) and for cyclobutanone (owing to steric effect of the ring).

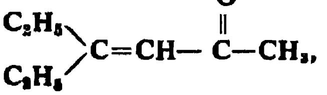
(*b*) **Testing Purity of a Sample.** Spectrum of a pure sample in general will display fairly sharp and well-resolved absorption bands. An impure sample will give broad and poorly resolved absorption bands. It is, however, not a very satisfactory method for testing purity of a sample.

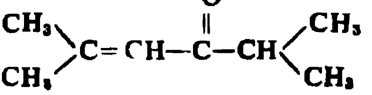
(*c*) **Study of Progress of a Reaction.** For example, progress of oxidation of a secondary alcohol to ketone is studied by getting IR spectra of test portions at different intervals. Here we expect disappearance of O—H stretching near 2·8 μm (~3570 cm^{-1}) and appearance of C=O stretchting near 5·8 μm (~ 1725 cm^{-1}).

Similarly progress of any chromatographic fractionation can be readily monitored by examining the IR spectra of the selected fractions.

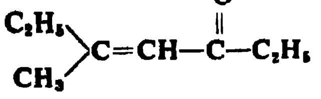
(*d*) **Establishing Identity of two Samples that have Identical Spectra in the same Medium.** The region 7—11 μm (1430—910 cm^{-1}) contains many absorptions caused by bending vibrations as well as those caused by stretching vibrations of C—C, C—O and C—N groups. This region of the spectrum is very rich in absorption bands, and shoulders since there are many more bending vibrations in a molecule than stretching vibrations. This region is, therefore, frequently termed. **Fingerprint region** . The region 2 5-7 μm (4000-1430 cm^{-1}) is) termed **Group frequency region.** The fingerprint region gives a good deal of information about the structure of the molecule, particularly about the patterns of substitution rather than the type of functional groups. Since no two compounds have absolutely identical IR spectra, a compound can be identified from its IR spectra just as a fingerprint can be used to identify a person.

Similar molecules may show very similar spectra in the group frequency region However, these will nearly always show discernible differences in the fingerprint region. For example, the isomers





and



have essentially identical UV spectra. Even IR spectra in the group frequency region are almost similar. These are identified from their IR spectra in the fingerprint region.

Table 12·2—Characteristic Infrared Absorption Bands of Functional Groups

Group	Frequency (wave number range cm^{-1})	Intensity*
1. Alkyl		
C—H (stretch)	2850-2960	(m—s)
Isopropyl,—CH(CH_3)$_2$	1380-1385 and 1365 1370	(s)
tert-Butyl,—C(CH_3)$_3$	1385-1395 and ∼1365	(m ; s)
2. Alkenyl		
$>$C—H (*stretch*)	3010-3100	(m)
C=C (*stretch*)	1620-1680	(v)
R—CH=CH_2	(Out-of-plane C—H bendings) 985-1000 and 905-920	(s)
R_2C=CH_2	880-900	(s)
cis RCH=CHR	675-730	(s)
trans RCH=CHR	960-975	(s)
3. Alkynyl		
≡C—H (*stretch*)	∼3300	(s)
C≡C (*stretch*)	2100-2260	(v)
4. Aromatic		(v)
Ar—H (*stretch*)	∼3030	(v)
C═C (*stretch*)	1500-1600	
Substituted aromatic ring (C—H-*out-of-plane bending*)		
Monosubstituted	690-710 and 730-770	(v,s)
o-Disubstituted	735-770	(s)
m- ,,	680-725 and 750-810	(s)
p- ,,	790-840	(s)
5. Alcohols, Phenols and Carboxylic acids		
OH (alcohols, phenols)	3200-3600	(broad, s)
OH (carboxylic acids)	2500-3000	(broad, s)
6. Aldehydes, Ketones, Esters and Carboxylic acids		
C=O (stretching)	1650-1750	(s)
7. Amines		
N—H	3300-3500	(m)
C—N	800-1300	(v)
8. Nitriles		
—C≡N	2200-2260	(m)
9. Nitro Compounds		
—NO_2	1330-1540	Pair of strong bands
10. Alkyl Halides		
C—F (stretching)	1000-1350	(s)
C—Cl (,,)	650-850	(s)
C—Br (,,)	515-690	
C—I (,,)	500-600	(s)

*Abberviations used : *s*=strong. *m*=medium, *v*=variable, ∼=approximately.

However, so many different absorptions occurring in the fingerprint region make the interpretation of IR spectra more difficult than interpretation in the group frequency region.

15. The Interpretation of Infrared Spectra.—No rigid rules exist for interpretation of a spectrum but certain general observations are helpful.

(1) Always begin at the high frequency end of the spectrum and use the fingerprint region only for confirmation.

For example. a strong band at 5·82 μm (1718 cm^{-1}) indicates almost certain presence of C=O group. It could be —CHO, >C=O, an acid, an ester or an amide.

(2) Total interpretation of the spectrum is seldom required and much valuable structural information being attained from relatively few bands. Only 10-20% bands can usually be assigned with certainty.

(3) Place more reliance on negative evidence, that is, the absence of absorption in a particular region than on positive evidence, that is, the presence of a band which may have several possible origins. For example, no absorption band in 1850-1587 cm^{-1} region shows absence of carbonyl group (C=O).

(4) The limits of published ranges of group frequencies are often defined by extreme cases of electronic influences. A compound with no such influence is expected to absorb towards the centre of the range quoted.

Infrared spectra of typical organic compounds are given below with interpretation of various absorption peaks in each.

(1) *n*-Octane (an Alkane)

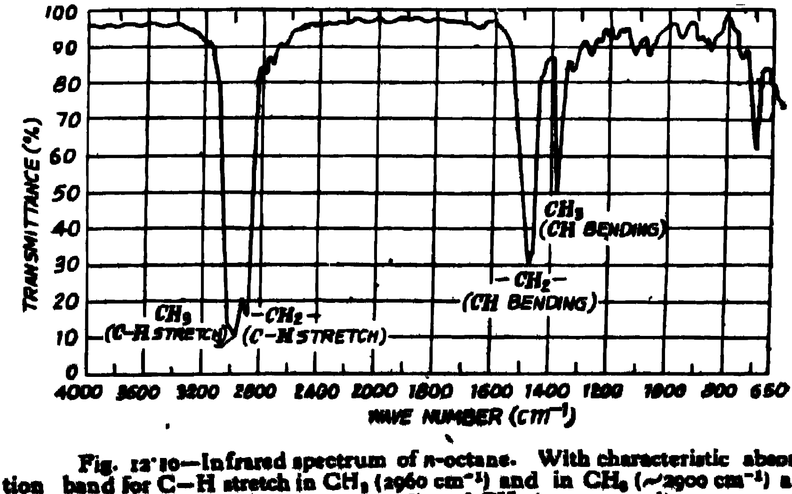


Fig. 12·10—Infrared spectrum of *n*-octane. With characteristic absorption band for C—H stretch in CH_3 (2960 cm^{-1}) and in CH_2 (~2900 cm^{-1}) and for C—H bending for CH_2 (~ 1375 cm^{-1}) and CH_3 (~1470 cm^{-1}).

(2) 1-Hexene (an alkene)

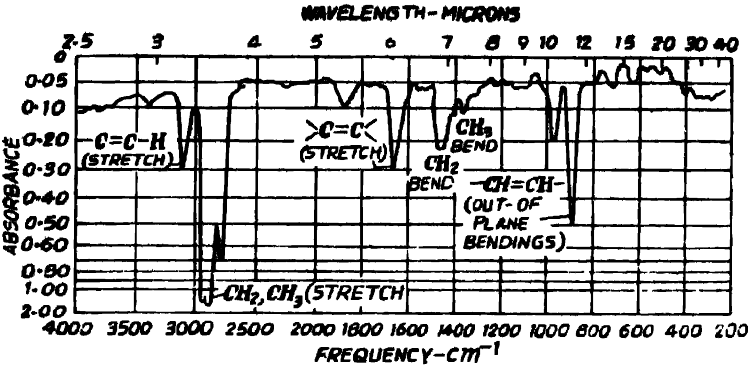


Fig. 12·11—Infrared spectrum of 1-hexene with characteristic absorption bands for >C—H stretching (~3050) ; C—H stretching in CH_3 and CH_2 (2850-2950 cm⁻¹) ; >C=C< (~ 1680 cm⁻¹) ; CH_2 bend (~1440 cm⁻¹) ; —CH=CH out-of-plane bendings (~910 and 990 cm⁻¹).

(3) 1-Hexyne (an alkyne)

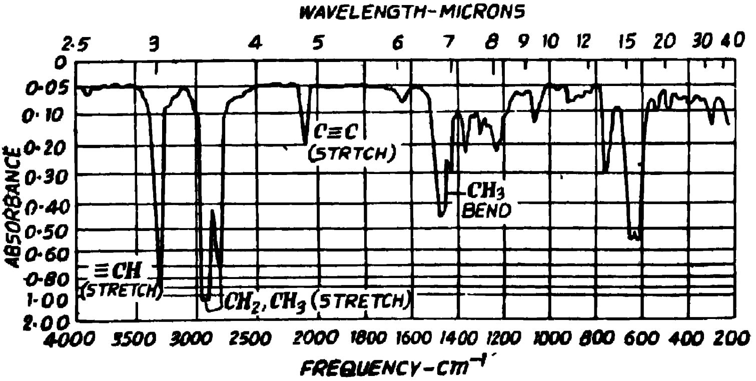
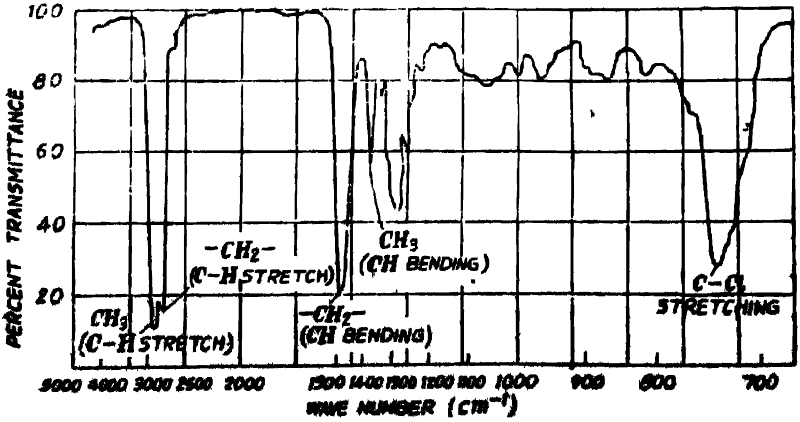


Fig. 12·12—Infrared spectrum of 1-hexyne with characteristic absorption bands for ≡C—H stretch (~3300 cm⁻¹) ; CH_2 and CH_3 stretch (~2880-2950) ; C≡C stretch (~2104 cm⁻¹) CH_2 bend (~1470 cm⁻¹)

(4) Chlorohexane (an alkyl halide)



(5) Toluene (monosubstituted benzene)

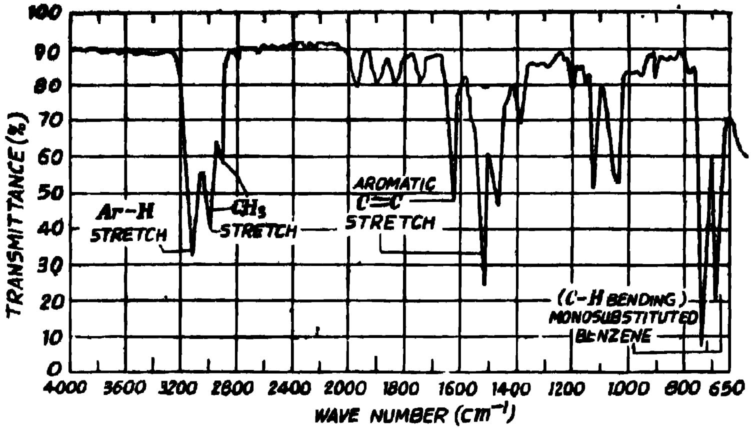


Fig. 12·14—Infrared spectrum of toluene.

In addition to the above disubstituted benzenes, xylenes show some characteristic absorption bands.

Ortho (735-770 cm^{-1}),

meta (680-725 and 750-810 cm^{-1}) and

para (790-810 cm^{-1}).

(6) Xylene (disubstituted benzene)

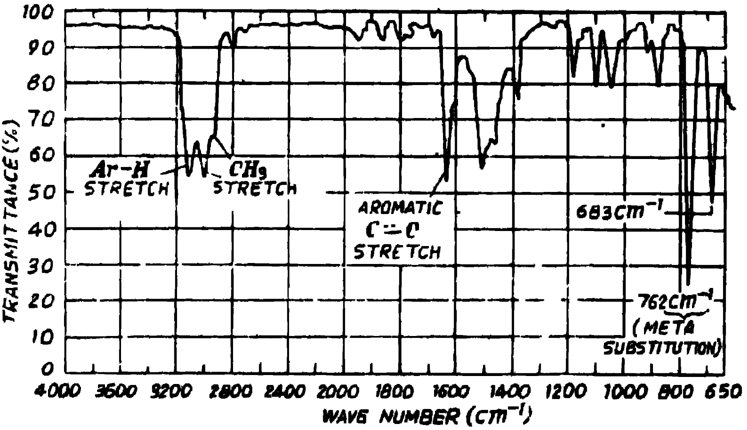


Fig. 12·15—Infrared spectrum of *m*-xylene.

SOLVED EXAMPLES

Example 12·3. *Identification of a hydrocarbon containing sevencarbon atoms from its spectrum (I) given* in Fig. 12·17.

Solution. Since the compound is a hydrocarbon, it is useful to begin with C—H stretching frequencies near 3000 cm^{-1}. There are no bands above this frequency, three types of hydrocarbons may, therefore, be ruled out : aromatic compounds (C—H stretch near 3030), alkynes (a strong band at 3300 cm^{-1}) and alkenes (C—H

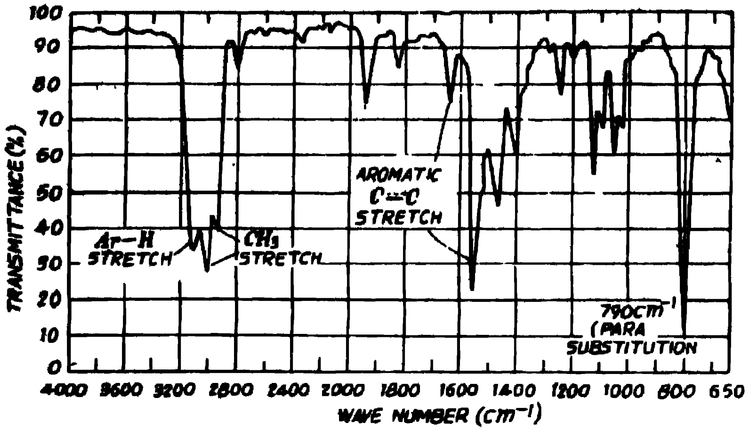


Fig. 12·16—Infrared spectrum of *p*-xylene

stretch lies between 3040 and 3010 cm^{-1}). The main bands at 2900 cm^{-1} clearly arise from C—H bond in a saturated hydrocarbon with smaller peaks at 2872 cm^{-1} on the side of the main band is due to symmetrical C—H stretch in a methyl group. As this band is not particularly strong, it suggests that only a small number of CH_3 groups are present.

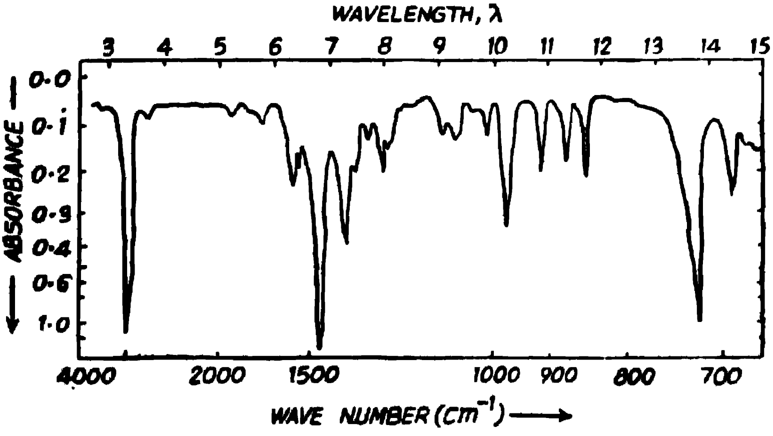


Fig. 12·17—Spectrum I.

The absence or only weak absorption from 1500-2500 cm^{-1} confirms the absence of acetylene or olefin C—H bonds. A strong band at 1450 cm^{-1} arises from the methylene scissoring vibration and is very strong in all aliphatic hydrocarbons. At 1460 cm^{-1}, the anti-symmetrical deformation of methyl group is also to be found as due to overlapping of $-CH_2$ vibration, no conclusion as to $-CH_3$ group can be drawn.

The given hydrocarbon is an alkane C_7H_{16} (heptane). The exact structure of heptane cannot, however, be predicted from the IR spectrum.

Example 12·4. *Identification of an organic compound from its IR spectrum (II) given below :*

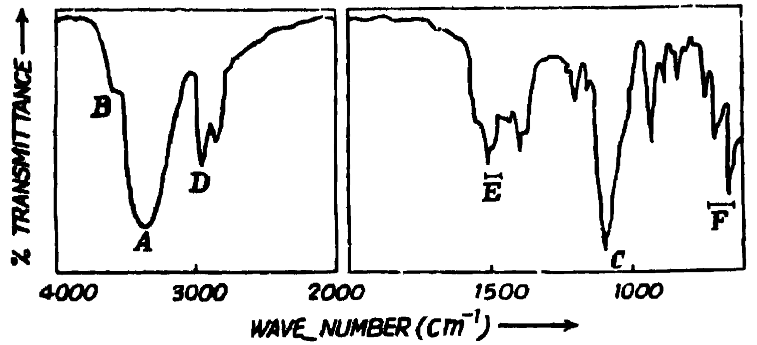


Fig 12·18—Spectrum II.

Solution.

The infrared spectrum II shows a strong band at 3350 cm^{-1} (A) with shoulder (B) at 3600 cm^{-1}, which strongly suggests an —OH group. This is confirmed by a very strong band at 1050 cm^{-1} (C) [see table on page 1·247]. The position of this band suggests that the compound is a primary alcohol. The presence of bands between 2900-3000 cm^{-1} (D) and between 1400-1450 cm^{-1} (E) and absence of absorptions ascribable to an aromatic nucleus between 3000-3100 cm^{-1} and 1500-1600 cm^{-1} indicates that the compound is an *aliphatic alcohol.*

Example 12·5. *Classify the compound from infrared spectrum III.*

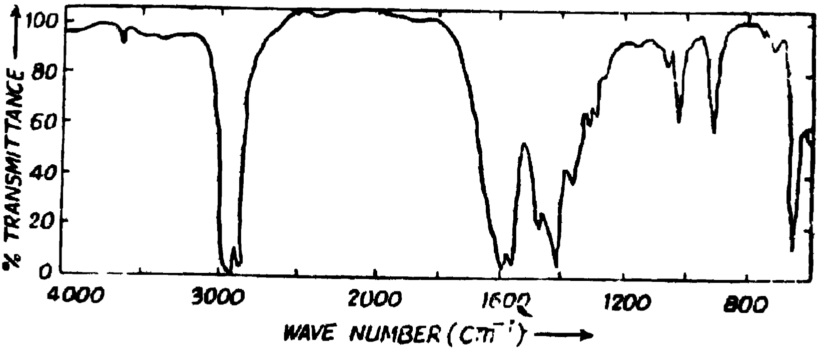


Fig. 12·19—Infrared Spectrum III.

[Hints. (i) Peak ~2900 cm^{-1} shows presence of alkyl group and absence of alkenyl, alkynyl and aryl groups.

(ii) Broad band between 2800-2950 cm^{-1} suggests OH group of carboxylic group.

(iii) Peaks (1550-1590 cm.$^{-1}$) due to C=O stretching suggest a carboxylate ion.

(iv) Peak at 1420-1460 cm^{-1} suggests CH stretching for CH_3 and CH_2

Ans. Salt of aliphatic acid.

Example 12·6. *Identify the compound $C_8H_8O_2$ from its infrared spectrum IV.*

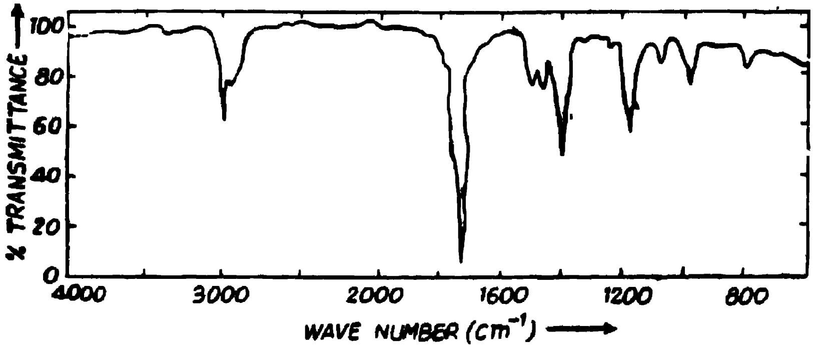


Fig. 12·2c—Infrared Spectrum IV.

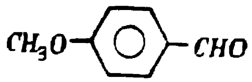
[**Hints.** (i) Peak at ~ 3030 cm^{-1} suggests it to be an aromatic compound.

(ii) Peak at ~ 1700 cm^{-1} suggests the presence of C=O (an aldehyde, ketone, acid or ester).

(iii) Peak ~ 1180 cm^{-1} suggests C—O—C stretching in an ether.

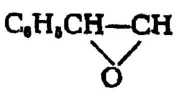
(iv) Small peak ~ 820 cm^{-1} suggests it to be a *p*-disubstituted compound.

The given compound is, therefore, *p*-methoxy-benzaldehyde.



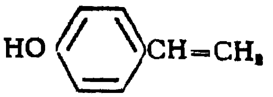
Example 12·7. *A compound of formula C_8H_8O has a strong infrared absorption band near 1690 cm^{-1}. Which of the following structures is the likely one for the compound :*

1. $C_6H_5.CH_2CHO$ 2. $C_6H_5OCH=CH_2$ 3.



$C_6H_5CH\underset{O}{—}CH_2$

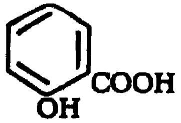
4. $C_6H_5COCH_3$ 5.



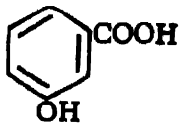
(**Ans.** C_6H_5 $COCH_3$. The band 1690 cm^{-1} is suggestive of conjugated carbonyl group in an aryl ketone.)

Example 12·8. *How would you differentiate between following pairs of compounds using infrared spectra :*

(i)



and



(ii) CH_3CH_2CHO
and
$CH_2{=}CH.CH_2OH$

[**Hint.** (i) the absorption peaks for OH and COOH in the ortho hydroxybenzoic acid will be 3550-3450 cm^{-1} (OH intramolecular hydrogen bonded), 3300-2500 cm^{-1} for COOH group, 755 cm^{-1} for 1 : 2 disubstitution and C—H stretching will be obtained.

In 3-hydroxybenzoic acid the absorption peaks will be observed at 780, 700, 880 cm^{-1} for C—H stretching ; $\sim$3610 for phenolic OH and 3300-2500 cm^{-1} for COOH.

(ii) CH_3CH_2CHO will show absorption bands at 1740-1720 cm^{-1} for C=O stretch ; 400-1000 cm^{-1} for C—CHO skeletal ;

$CH_2{=}CH{-}CH_2OH$ will have absorption bands at $\sim$1050 cm^{-1} for primary alcohol (C—O stretching and bending) and $\sim$9·50 for vinyl group, $CH_2{=}CH$—(C—H stretching), 3100-3000 cm^{-1} for C=C bond (=C—H stretching)

Example 12·9. *An organic compound with molecular formula* C_8H_6 *decolorises bromine in carbon tetrachloride and gives a white precipitate with ammoniacal silver nitrate solution. Its IR spectrum V is shown in Fig 12·21. Identify the compound.*

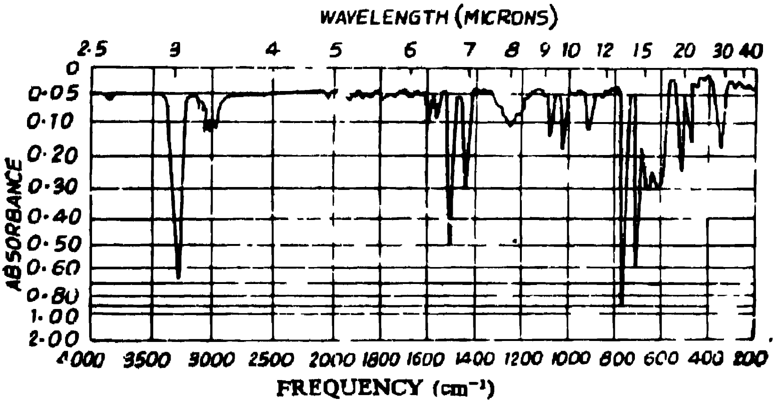


Fig. 12·21—IR spectrum V

[**Hint.** (i) Reaction with Br shows it to be unsaturated.

(ii) Reaction with $AgNO_3$ shows it to be 1-alkyne.

(iii) Peak at $\sim$ 3300 cm^{-1} shows the presence of alkynyl group.

(iv) Peak at $\sim$ 3030 suggests the presence of aryl group. This is further confirmed by the peak ($\sim$ 1500 cm^{-}) due to C$\cdots$C stretch.

(v) Peak at 770 cm^{-1} suggests it to be monosubstituted benzene.

Structure of the compound C_8H_6 deduced from (i) to (v) is phenylacetylene.

$$C_6H_5{-}C{\equiv}CH$$

TABLE 12·3—CHARACTERISTIC INFRARED ABSORPTION BANDS

Absorption intensity symbols : *s*=strong, *m*=medium, *w*=weak, *v*=variable, *b*=broad, *sh*=sharp.

Spectral region cm⁻¹	*Vibrational Classification*	*Group and Environments*	*Wave-number cm⁻¹*	*Wavelength µm*	*Intensity*
3700—3333	O—H stretching				
	(1) Free	Alcohols and phenols			
		(*a*) primary alcohol	~3046	~2·75	*v*
		(*b*) secondary alcohol	~3630	~2·76	*s*
		(*c*) tertiary alcohol	~3620	~2·76	*s*
		(*d*) phenol	~3610	~2·77	*sh*
	(2)	Intermolecularly hydrogen bonded (changes on dilution)			*s*
	(3)	Single bridged compound	3450	b	
		(*a*) Dimeric association	3400	...	
		(*b*) Polymeric association	3200	2·78—3·23	*b*
	(4)	Water of crystallisation	3600—300		*w*
3550—3000	N—H stretching				
	(1) Free	Primary amine	~3500	2·86	*w*
		Secondary amine	~3450	2·90	*w*
	(2)	Associated	3350	2·99—3·23	
3300	≡C—H stretching	Alkyne	3300	3·03	*s*, *sh*
3200—2850	O—H stretching (a)	Alcohols and phenols hydrogen bonded			
		(*i*) Intramolecular	3200	3·13—4·00	*b*
		(*ii*) Conjugate chelate	2900	,,	*b*

Spectral region	*Vibrational Classification*	*Group and Environment*	*Wave number cm^{-1}*	*Wavelength µm*	*Intensity*
	O—H stretching (b)	Carboxylic acid $\overset{\diagup O}{\mathrm{C}}\mathrm{—O—H}$ dimer (confirmed by C=O)	3200—2850	3·03—4·00	*b*
3100—3000	=C—H stretching	Alkane or arene			
		(i) Monosubstituted 2 band (Vinyl)	3095—3075 3040—3010		*m* *m*
		(ii) Disubstituted (gem)	3095—3075		*m*
		(iii) Disubstituted cis & trans.	3040—3010 3030		*m* *v*
3000—2850	C—H stretching	Alkyl group, CH_3, CH_2, CH 2 bands			Region not fully resolved by NaCl prism spectrometer. Intensity of CH_3 asym $>CH_2$ asym
		CH_3 asymmetric	2975—2950	3·36—3·39	
		CH_2 ,,	2940—2915	3·40—3·43	
		CH_3 symmetric	2885—2860	3·47—3·50	
		CH_2 ,,	2870—2845	3·48—3·52	
2900—2700	C—H stretching of $\overset{\diagup O}{\mathrm{—C—H}}$	Aldehyde 2 bands	2900—2820 2775—2700	3·5 —3·7	*m, sh* (a band *w* at 2725 is diagnostic for aldehydes)
2500—2200	C≡C stretching	Alkyne RC≡CH	2260	4·42—4·65	*w*
		Disubstituted R—C≡CR	2190		*v* *w*
2000—1750	C=O stretching	Anhydride	1870—1820		*s*
		(i) Saturated 6 membered ring.	1800—1750		*s*
		(ii) Saturated acyclic	1792—1740 1830—1780		*s* *s*
		(iii) Unsaturated and aryl, acyclic	1770—1720		*s*
		Acid chloride $\mathrm{RC}\overset{\diagup O}{\underset{\diagdown Cl}{}}$	1800—1790		*v.s.*

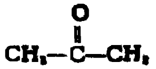
Spectral region	*Vibrational Classification*	*Group and Environment*	*Wave-number cm⁻¹*	*Wavelength µm*	*Intensity*
1750—1660	C=O stretching	Acid $\mathrm{R-\overset{O}{C}-OH}$			
		(*i*) saturated aliphatic	1725—1700	5·80—5·88	*v.s*
		(*ii*) α, β-unsat. aliph. C=C	1715—1690	5·83—5·92	*b, .rough*
		(*iii*) aryl	1700—1680	5·88—5·95	*b, ,,*
	C=O stretching	Ketones	1725—1705		
		(*i*) Saturated acyclic			
		(*ii*) Saturated cyclic	1725—1705		
		(*iii*) α, β-unsaturated	1685—1665		
		5 or 6 membered ring			
		(*iv*) aryl	1700—1680		
	C=Ostretching	Aldehydes (*i*) Aliphatic	1740—1720	5·75—5·81	*s*
		(*ii*) Aromatic	1715—1695	5·83—5·90	*s*
	C=O stretching	Esters $\mathrm{R\overset{O}{C}-OR}$	1745—1725	5·73—5·80	*v.s.*
1700—1680					
1650—1450	C=O stretching	Amide $\mathrm{R\overset{O}{C}-NH_2}$	~1650	5·88—5·99	*v.s.*
	C=O stretching	(*a*) β-ketoesters	~1650	~6·06	*s*
		(*b*) Carboxylate anion	1610—1550	6·21—6·45	*s*
	C=C stretching	Alkenes	1680—1620	5·95—6·17	*v*
		(*a*) non-conjugated			
		(*b*) Mono-substituted vinyl	~1645	~6·08	*m*
		Aromatic (Arene)	~1600	~6·25	*v*
		Characteristic bands due	1580	~6·33	*v*
		to skeletal carbon stretch-	1500	~6·67	*m*
		ing vibration.	1450	~6·90	*m*

The C=O stretching is shifted to lower frequencies by as much as 25 cm⁻¹ when conjugated.

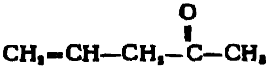
Spectral region	*Vibrational Classification*	*Group and Environment*	*Wave-number cm^{-1}*	*Wavelength µm*	*Intensity*
1480—1415	C—H bending	Alkyl group			
		CH_3 asymmetric	1470—1435	6·80—6·97	s
		CH_2 symmetric	1480—1440	6·76—6·94	s
					s
1385—1340	C—H bending	alkyl group			
		CH_3 symmetric	1385—1370	7·25—7·30	s
		C—H	~ 1340	~7·46	w
1300—1150	C—O—C stretching	Ethers. Aryl (unsaturated)	1270—1230		
		Aliphatic	1150—1060		
	C—O stretching and O—H bending	Phenols ArOH	~ 1230	~8·3	s
1150—1050	C—O stretching and bending	Alcohols Tertiary	~ 1150	~8·64	s
		Alcohols Secondary	~ 1100	~9·09	s
		Alcohols Primary	~1050	~9·52	s
955—690	C—H stretching	Vinyl group $CH_2=CH—$	955	10·05	s
			910	11·05	s
	C—H stretching	R $CH=CR_2$	840—790	11·9—12·7	s
	C—H stretching	1 : 4-disubstituted benzene	835—810	12·00—12·35	s
		1 : 3 ,, ,,	810—750	12·35—13·33	s
			710—690		
	C—H stretching	mono-substituted benzene	770—730	12·99—13·70	s
		1 : 2-disubstituted	770—735	12·99—13·61	

Answer the following Questions :

1. Give approximate position of the characteristic infrared bands in the following compounds.

(i) 

$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

(ii) 

$CH_2=CH-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

(iii) CH_3CH_2OH. *(Guru Nanak Dev B.Sc., 1977)*

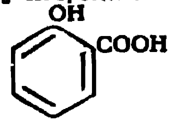
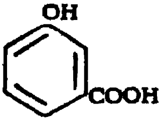
2. Discuss the principle of infrared spectrum. *(Guru Nanak Dev. B.Sc., 1977)*

3. Discuss briefly the underlying principle in the detection of organic compounds by IR spectroscopy. *(Delhi B.Sc. Hons. 1976)*

4. How are the structures of the following compounds indicated in the IR spectral data :

(i) Actophenone ; (ii) 1-Butene ; (iii) Propionamide ; (iv) Phenol ? *(Delhi B.Sc. Hons. 1976)*

5. How will you differentiate between the following pairs of compounds using IR spectra ?

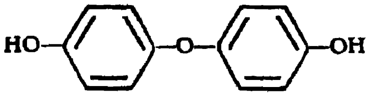
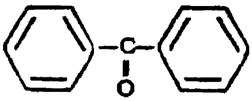
(i)  and 

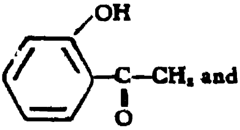
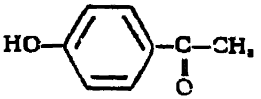
(ii) CH_3-CH_2-CHO and $CH_2=CH-CH_2-OH$ *(Delhi B.Sc. Hons. 1977)*

6. How can spectral data be helpful in indicating the structure of the following compounds :

(a) Cyclohexanone, (b) 2-Cyclohexen-1-one,
(c) Benzaldehyde, (d) Ethyl alcohol,
(e) Acetic acid ? *(Delhi B.Sc. Hons. 1975)*

7. How will infrared spectral data be useful to distinguish the compounds in the following pairs :

(i)  and 

(ii)  and 

(Delhi B.Sc. Hons. 1973)

8. What information can you obtain about the following compounds by the application of UV and IR spectroscopy :

(i) Acetophenone, (ii) Cinnamic acid, (iii) Phenol and (iv) Benzamide ? *(Delhi B.Sc. Hons. 1972)*

9. Compound A, molecular formula C_4H_6 has λ_{max} 217 µm. On controlled hydrogenation it adds one mole of hydrogen to give the compound B which shows absorption at 1650 cm^{-1} (6·06 µm). Under acidic conditions B adds a mole of water to give the compound C which can be oxidised to compound D. C shows absorption at 3650 cm^{-1} (2·75 µm) and D at 1715 cm^{-1}

(5·83μm). The compound D undergoes haloform reaction to yield propionic acid. What are the structures for the compounds A, B, C, and D ? Give the chemical reactions involved. What functional groups are associated with the spectroscopic data given above ? (*Delhi B.Sc. Hons.* 1972)

10. Which of the following compounds do not absorb light above 2000Å ?

(i) *n*-Propyl alcohol, (ii) Benzene,
(iii) Diethyl ether, (iv) Methyl vinyl ketone,
(v) Methyl alcohol. (*Osmania B.Sc.* 1975)

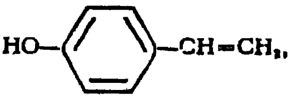
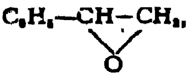
11. Account for the fact—Infrared carbonyl frequency in salicylaldehyde is lower than that of *m*-hydroxybenzaldehyde. (*Osmania B.Sc.* 1975)

12. Give the type of IR absorption band you will look for to distinguish between the following pairs of compounds :

(*a*) $CH_3-C\equiv C-CH_3$ and $CH_3-CH_2-C\equiv CH$
(*b*) CH_3CH_2OH and CH_3COOH
(*c*) $(CH_3)_3N$ and $(CH_3)_2CHNH_2$
(*d*) $CH_3.CH_2.CH_2.CH_3$ and $CH_3.CH_2.CH=CH_2$
(*e*) $CH_3.CH_2.CHO$ and $CH_3.CO.CH_3$
(*f*) $C_6H_5.C\equiv CH$ and $C_6H_5.CH=CH_2$
(*g*) CH_3COOH and $CH_3COOC_2H_5$
(*h*) $CH_3.CH_2.C\equiv N$ and $CH_3.CH_2.C\equiv CH$.

13. An organic compound having molecular formula C_8H_8O has a strong IR absorption band near 1690 cm^{-1}. Assign a structure to it. Different isomers of the formula C_8H_8O are :

(i) $C_6H_5CH_2CHO$, (ii) $C_6H_5COCH_3$,

(iii)  (iv) 

$C_6H_5-\underset{\diagdown O \diagup}{CH-CH_2}$,

(v) $C_6H_5O-CH=CH_2$.

14. Two isomers A and B of the molecular formula C_3H_6O give IR absorption band near 1650 cm^{-1} and 1710 cm^{-1} respectively. Assig. structural formulae to A and B consistent with their IR absorption bands.

15. IR spectrum of acetone gives two maxima due to C—H vibration at 1360 cm^{-1} and 3000 cm^{-1}. Identify the stretching and bending mode. Express the maxima in μ units. (*Delhi B.Sc. Hons.* 1978)

16. Using IR spectroscopy show how you could distinguish between—
(i) *o*- and *p*-HOC_6H_4CHO
(ii) $C_6H_5COC_2H_5$ and *p*-$CH_3C_6H_4COCH_3$. (*Delhi B.Sc. Hons* 1979)

17. Illustrate the importance of IR spectroscopy to organic chemists. (*Delhi B.Sc. Hons.* 1980)

HINTS AND ANSWERS

1. (i) C—H stretching peak at 2962—2853 cm^{-1}
C=O stretching peak at 1725—1705 cm^{-1}
(ii) =C—H stretching peak at 3040—3010 cm^{-1} ;
C—H and C=O stretching peaks as in (i) above ;
C=C stretching peak at 1650 cm^{-1}

(*iii*) O—H stretching peak at 3650—3590 cm^{-1}
C—H stretching peak as above.

4. (*i*) *Acetophenone* : Characteristic peak for
C=O stretching at 1725—1705 cm^{-1}
C—H (aromatic) stretching at ~750 cm^{-1}

(*ii*) *1-Butene* : C—H stretching peak at 3040—3010 cm^{-1} ; C—H stretching peak at 2962—2858 cm^{-1} ; C=C stretching peak at 1650 cm^{-1}

(*iii*) *Propionamide* : >C=O stretching peak at 1690—1650 cm^{-1}; *N—H stretching peaks at ~3500 and 3400 cm^{-1}; N—H bending at 1620—1590 cm^{-1}*

(*iv*) *Phenol* : C—H (aromatic) stretching at ~750 cm^{-1} ; O—H stretching at 3650—3590 cm^{-1} ; C—O stretching at 1410—1310 cm^{-1}

5. **Hints.** (*i*) In IR, O—H stretching for first at 3200—2500 cm^{-1} (weak band and broad). For second at 3400—3200 cm^{-1} (strong and broad).

(*ii*) In first IR signals for C=O stretching, and C—H stretching.

In second IR signals for O—H stretching C—O stretching, and =C—H stretching.

6. (*a*) C=O stretching (IR peak)

(*b*) UV absorption due to conjugation [absent in (*a*)]. IR peaks for C=O stretching ; =C—H stretching and C=C stretching ;

(*c*) IR absorption for $-\underset{\underset{H}{|}}{C}=O$ at 1740—1720 cm^{-1} ; =C—H (aromatic)

(*d*) IR absorption for C—H stretching, O—H stretching and C—O stretching. It is transparent to UV.

(*e*) IR absorption for C=O stretching, O—H stretching and C—H stretching.

7. (*i*) In the first IR spectrum will show peaks for O—H stretching C—H (arom) stretching, and C—O stretching.

In second peaks for C=O stretching, C—H (arom).

(*ii*) In first O—H (chelated) stretching at 3200—2500 cm^{-1}, C=O (chelated) stretching at ~1640 cm^{-1}.

In second O—H stretching (free) at 3400—3200 cm^{-1} ; C=O (free) at 1700—1580 cm^{-1}.

8. (*i*) *Acetophenone* : Extended conjugation in benzene and C=O group shown by UV. In IR spectrum C=O stretching and C—H (arom) stretching.

(*ii*) *Cinnamic acid* : Extended conjugation with 2 (=) bonds outside benzene ring shown by UV.

In IR spectrum peak for C—H (arom), =C—H, C=O, C—O and O—H

(*iii*) *Phenol* : In UV for benezene ring. IR for O—H, C—O, C—H(arom)

(*iv*) *Benzamide* : UV for extended conjugation.

IR for C=O stretching, N—H stretching, N—H bending, C—H (arom).

9. (*i*) C_4H_6 (A) may be an alkyne or a diene.

(ii) UV λ_{max} 217 μ indicates the presence of a conjugated double bond. So A can be 1, 3-butadiene, $CH_2{=}CH{-}CH{=}CH_2$.

(iii) On hydrogenation there is 1 : 4 addition to give 2-Butene,

$$CH_3{-}CH{=}CH{-}CH_3 \quad (B)$$

This is shown by IR λ_{max} 1650 cm^{-1} for C=C stretching.

(iv) Addition of water molecule to B gives $CH_3{-}CH_2{-}CHOH{-}CH_3$ 2-Butanol (C). This is shown by O—H stretching at 3650 cm^{-1}

(v) C on oxidation gives $CH_3{-}CH_2{-}\underset{\|}{\underset{O}{C}}{-}CH_3$ (D) as is indicated by *IR absorption at 1715 cm^{-1} for C=O stretching.*

(vi) Structure of D is confirmed as it gives haloform reaction and yields propionic acid. The products show the presence of $CH_3{-}C{=}O$ group.

10. Above 2000 Å is UV region.

(i) (iii) and (v) do not absorb light in this region.

11. In salicylaldehyde there is chelation between C=O and or the OH group. This is absent in *m*-hydroxybenzaldehyde.

12 Only a representative band is given in each case.

(*a*) ≡C—H stretch (~3300 cm^{-1})

(*b*) C=O stretch (~1760 cm^{-1})

(*c*) N—H stretch (~3500—3400 cm^{-1})

(*d*) C=C stretch (~1645 cm^{-1}) ; C—H stretch of 1-alkene (~3100 cm^{-1}) ; $CH_2{=}CH_2$ bend (~995, 915 and 1410 cm^{-1}).

(*e*) C—H stretch of formyl group (~2850 and 2770 cm^{-1})

(*f*) ≡CH stretch (~3300 cm^{-1})

(*g*) Very broad O—H stretch (~2900 cm^{-1})

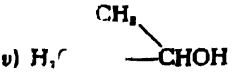
(*h*) ≡C—H stretch (~3300 cm^{-1}).

13. $C_6H_5COCH_3$ (Acetophenone)—The IR absorption band near 1690 cm^{-1} suggests the presence of a conjugated carbonyl group.

14. Various isomers of the formula C_3H_6O are :

(i) $CH_2{=}CH{-}CH_2OH$, (ii) $CH_3{-}CO{-}CH_3$

(iii) $CH_3.CH_2$ CHO and (iv)



$H_3C{-}\overset{CH_3}{CHOH}$

A is (i) IR absorption band near 1650 c

B is (ii) IR absorption band near 1710 cn

(iii) Gives IR band near 1740 cm^{-1} and

(iv) would not give IR band near 1650 cm^{-1}—these are, therefore, ruled out.

15. C—H stretching at 3000 cm^{-1} and C—H bending at 1360 cm^{-1}

3000 cm^{-1}=3·33 μ ; 1360 cm^{-1}=7·35μ

16. Hints. (*i*) *o*- gives O—H stretching band at ~ 3200 cm^{-1} due to intramolecular hydrogen bonding. *p*- gives it at ~ 3610 cm^{-1} due to intermolecular hydrogen bonding.

(*ii*) *p*-$CH_3C_6H_4COCH_3$ shows additional characteristic band due to para di-substitution at ~ 810-835 cm^{-1}.

NUCLEAR MAGNETIC RESONANCE (NMR) SPECTROSCOPY

16. Introduction.—Nuclear magnetic resonance spectroscopy is useful in detecting and distinguishing between nuclear particles present in a sample. The fundamental concept of it is that an alternating magnetic field can induce transitions between the spin levels of a nucleus placed in a fixed magnetic field. In this respect NMR spectroscopy differs from ultraviolet and infrared spectroscopy which analyse light and often radiations emitted or absorbed by electrons surrounding the nucleus.

17. Origin of Spectra.—The nuclei of those isotopes which possess an odd number of protons or an odd number of neutrons or both show spin phenomenon and are associated with angular momentum. The momentum is characterised by a molecular spin quantum number '*I*' such as $I=\frac{1}{2}n$ ($n=0, 1, 2, 3$......etc).

Those nuclei which have $I=0$, do not possess angular momentum and NMR phenomenon cannot be observed for them. The nuclei of ^{14}C, ^{16}O fall into this class. Nuclei for which $I=\frac{1}{2}$ include H, ^{19}F, ^{13}C, ^{31}P and ^{15}N, whereas ^{2}H and ^{14}N have $I=1$, Boron, ^{11}B has nucleus for which $I=\frac{3}{2}$.

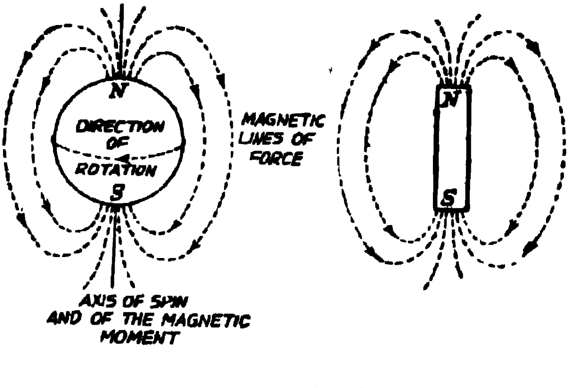


Fig. 12·22—Spinning proton is associated with a magnetic field, i.e., it resembles a bar magnet.

Since atomic nuclei are associated with charge, a spinning nucleus gives rise to an electric current and thus has a magnetic field associated with it.

Simplest nucleus is a proton. We limit our discussion to the magnetic spectra that arise from proton alone. This spectra is termed Proton Magnetic Resonance (PMR) spectra.

18. The Nucleus in a Magnetic Field.—When a spinning proton is placed in a magnetic field H_0, it' magnetic moment H may be aligned with the external magnetic field H_0 or against it. The two alignments are not of equal energy. Energy of the proton (*a*) aligned with the magnetic field is lower than the proton (*b*) which is aligned against the magnetic field.

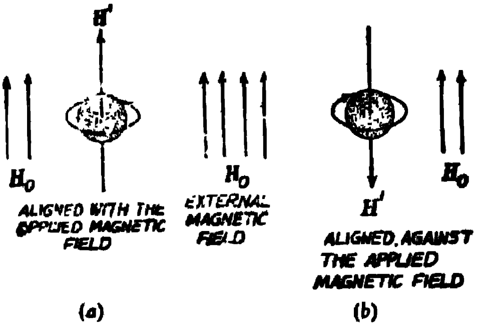

H'
H_0
ALIGNED WITH THE APPLIED MAGNETIC FIELD
H_0
EXTERNAL MAGNETIC FIELD
H'
H_0
ALIGNED AGAINST THE APPLIED MAGNETIC FIELD
(a)
(b)

Fig. 12·23—The two orientations of the magnetic moment of a proton in an external magnetic field H_0.

When a spinning nucleus is placed in an external magnetic field, *i.e.*, between the poles of a large magnet, the field exerts a torque upon the spinning nucleus and the nucleus tends to align its magnetic field with the external field. As only definite orientations of magnetic field of the nucleus with respect to the external magnetic field are permitted by quantum theory, the nucleus may begin to precess around the direction of the applied external magnetic field. In doing so the axis of the nucleus tilts in addition to spinning around its axis and carries out a slow rotation around the direction of the external field. The rate of precession increases rapidly with stronger disturbing torque and stronger magnetic field. For example, hydrogen nuclei when placed in a strong magnetic field of 10,000 gauss, precess 42 million times (42 Mc—megacycles) per second. Most magnetic nuclei have precessing frequencies between 0·1 and 40 Mc for fields from 1,000 to 10,000 gauss.

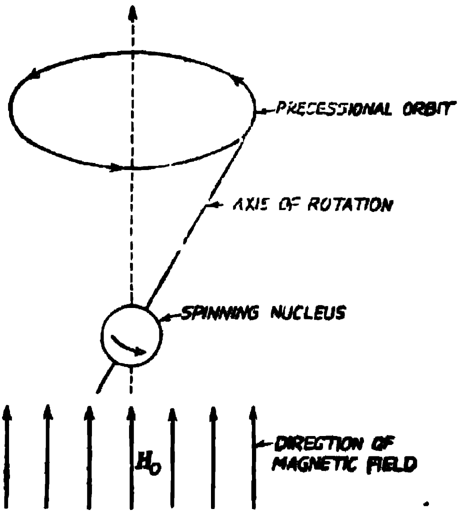


Fig. 12·24—The Nucleus precessing a Magnetic Field, H_0.

19. Nuclear Magnetic Resonance.—Information about precession is transmitted outside the sample by exciting the nuclei with a second, small rotating radiofrequency (R-F) field *applied perpendicular to the stationary magnetic field, H_0 and alternating at the frequency with which the nuclear axis precesses.*

The stationary magnetic field H_0 gets the spinning nuclei line up and precess at the alternating R-F in the direction perpendicular to H_0 and superimposed over stationary field, causes the nuclei to wobble in rhythm, *i.e.*, in resonance from the *Z* direction.

Nothing will happen as long as the frequency of precession of the nucleus and the frequency of rotation of R-F are different because of the cancelling torque applied to the nuclear axis. But when the R-F field rotates at exactly the frequency of the nuclear precession, a constant additional torque is applied which causes the nucleus to flip (tilt) from one angle of precession to another about the H_0. The energy required to alter the precessional frequency is supplied from R-F field whenever it is exactly in resonance with precession.

The detection of the change in the precessional frequency is based upon electro-magnetic induction (the sample under observation is surrounded by a few turns of wire with its axis parallel to the *y*-axis). The resulting nuclear magnetic moments are capable of inducing a small but detectable R-F voltage across the terminals of the coil.

Since atomic nuclei are associated with charge, a spinning nucleus gives rise to an electric current and this has a magnetic field associated with it. The magnitude of the magnetic dipole (μ) is a characteristic value for a given nucleus. When a spinning nucleus is placed in a uniform magnetic field H_0 the nuclear magnet experiences a torque which tends to align it with the field, and because of the interaction of the nucleus with the main magnetic field, the spinning nucleus precesses about the field direction. Quantum mechanical calculations show that the allowed orientations of the nuclear magnet with respect to the field direction are given by $2I+1$, so that for the proton only two orientations and thus two energy levels are possible. These levels may be regarded as alignment of the nucleus with the field (low energy) and against the field. The energy separation is given by

$$\Delta E = \frac{\gamma h H_0}{2\pi} \qquad \ldots(i)$$

When a small magnetic field is applied at 'right' angle to the main magnetic field, the spinning nucleus will be tipped out of the main field at one instant, but half a cycle later in the precession, the nucleus would be tipped back into the main field. The net result is no change. But if the secondary field rotates at exactly the same rate as the nucleus precesses, the nucleus will always be tipped off out of the new field (faster or slower speeds of rotation of the tipping field will have no effect) and transfer of energy from the tipping field to the nucleus occurs. The effect is termed *nuclear magnetic resonance.*

The energy absorbed by the nucleus is used to promote it to a higher energy state and to satisfy the equation

$$E = h\nu \qquad \ldots(ii)$$

The frequency of the electromagnetic radiation used for tipping field lies in the radiofrequency range. For protons on the main magnetic field of 14092 gauss, the frequency required for resonance is 60 megacycles per sec (Mcps).

$$1 \text{ Mc} = 10^6 \text{ cycles}.$$

From the equations (i) and (ii) it follows that

$$\nu = \frac{\gamma H_0}{2\pi}.$$

where γ is a nuclear constant called gyromagnetic ratio which has different values for different nuclei. For a proton, $\gamma = 26750$.

Though in principle it is possible to maintain the main magnetic field H_0 and vary the frequency ν of tipping field until the resonance condition is achieved, it is simpler to keep ν constant and vary the main magnetic field. Therefore a *pmr* spectrum is a plot of intensity of absorption along the ordinate against field strength as abscissa.

20. PMR Spectrometer.—An NMR spectrometer consists basically of a magnet, radiofrequency (R-F) transmitter or oscillator and a suitable detector. When a sample comprising atoms having nuclei with certain magnetic properties is placed in the magnetic pole gap and subjected to R-F field of the oscillator, absorption of R-F energy (resonance) occurs at particular combinations of the oscillator frequency and magnetic field strength and an R-F signal is picked up by the detector.

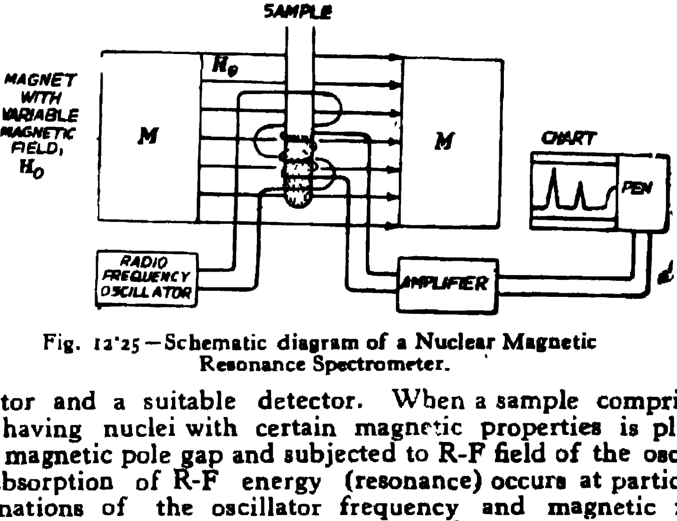

SAMPLE
MAGNET WITH VARIABLE MAGNETIC FIELD, H_0
H_0
M
M
CHART
PEN
RADIO FREQUENCY OSCILLATOR
AMPLIFIER

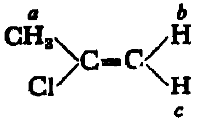
Fig. 12·25—Schematic diagram of a Nuclear Magnetic Resonance Spectrometer.

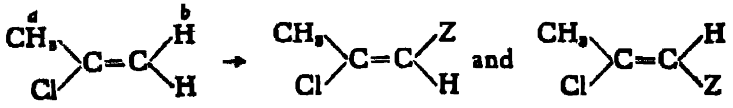
21. Number of signals obtained from a sample.—Absorption of R-F energy by a proton depends on its local environments such as electron density at it and the presence of other protons in its neighbourhood. *A set of protons with identical environment absorbed R-F energy at the same field strength and are termed* **equivalent.** All of them will give only one *pmr* signal. *Protons with different environments are referred to as* **non-equivalent.** Each one of these will give one *pmr* signal. So the number of *pmr* signals equals the number of non-equivalent protons.

Equivalence of protons can be judged by replacing them one by one by a substituent Z. If the products obtained are identical or enantiomers (mirror images), the protons are equivalent otherwise not. For example in ethyl bromide, $CH_3—CH_2—Br$, we have three methyl protons and two methylene protons. Three methyl protons are equivalent because replacement of any one of the three hydrogen atoms gives the same product $Z—CH_2—CH_2—Br$. Similarly, two methylene protons are equivalent because substitution of any one of these gives the same product, $CH_3—CHZ—Br$. However, 3 methyl protons differ from the 2 methylene protons since $Z\text{-}CH_2—CH_2—Br$ and $CH_3—CHZ—Br$ are different products. Thus $CH_3—CH_2—Br$ gives two *pmr* signals—one of these given by 3 equivalent methyl protons and the other given by 2 equivalent methylene protons.

Proceeding along these lines we can decide whether the given set of protons are equivalent or not and therefrom calculate the number of *pmr* signals. A few more examples are given below :

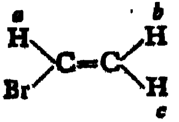
Compound	*Nature of protons and number of pmr signals*
$\overset{a}{CH_3}—\overset{b}{CH_2}—\overset{c}{OH}$ Ethanol	Three types of protons : (*a*) in CH_3, (*b*) in CH_2 and (*c*) in OH *Three pmr signals*
$\overset{a}{CH_3}—\overset{b}{CHCl}—\overset{a}{CH_3}$ 2-chloropropane	Two types of protons (*a*) and (*b*) *Two pmr signals*
$\overset{a}{CH_3}—\overset{b}{CH_2}—\overset{c}{CH_2}—Br$ 1-Bromopropane	Three types of protons : (*a*), (*b*), (*c*) *Three pmr signals*

In 2-chloro-1-propene,  , there are three types of protons since the two vinylic protons *b* and *c* are not equivalent—the replacement of either of these would yield a pair of diastereoisomeric products given below :

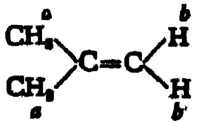


(2-chloroprop-l-ene A pair of diastereoisomeric products)

Similarly, in vinyl bromide there are three kinds of protons marked *a*, *b* and *c*. 2-chloro-l-propene and vinyl bromide both will, therefore, give three *pmr* signals. In 2 methyl-1-propene, however, there are only two kinds of protons marked *a* and *b*. It will give two *pmr* signals.



Vinyl bromide



2-Methyl-l-propene

Problem 12·1. How many different sets of equivalent protons do each of the following compounds have? How many signals would you expect from each compound in its spectrum?

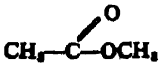
(*i*) CH_3-CH_3

(*ii*) $CH_3-CH_2-CH_3$

(*iii*) CH_3-O-CH_3

(*iv*) $CH_3-CBr_2-CH_3$

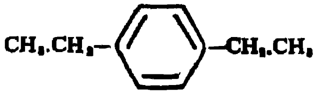
(*v*)



$CH_3-\overset{O}{C}-OCH_3$

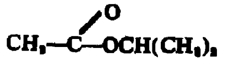
(*vi*) $CH_3.CHClCH_2Cl$

(*vii*)



(*viii*) CH_3CHO

(*ix*)



$CH_3-\overset{O}{C}-OCH(CH_3)_2$

(*x*) CH_3CH_2OH

Ans. (*i*) one ; (*ii*) two ; (*iii*) one ; (*iv*) one ; (*v*) two ; (*vi*) three ; (*vii*) three ; (*viii*) two ; (*ix*) three , (*x*) three

22 Position of signals and chemical shift.—When a molecule is placed in a magnetic field, its electrons circulate and thus generate a magnetic field termed induced magnetic field which may either reinforce or oppose the applied magnetic field. If the induced field opposes the applied field, the proton requires a stronger magnetic field to give a *pmr* signal. The proton is said **to be shielded**. The shielded proton requiring a stronger magnetic field for giving the *pmr* signal is said to absorb **upfield**.

In case the induced field reinforces the applied magnetic field, the effective field strength which the proton experiences increases. The proton is said to be **deshielded** and it requires only a smaller applied field to give a *pmr* signal and since it requires only a smaller applied magnetic field, it is said to absorb **downfield**.

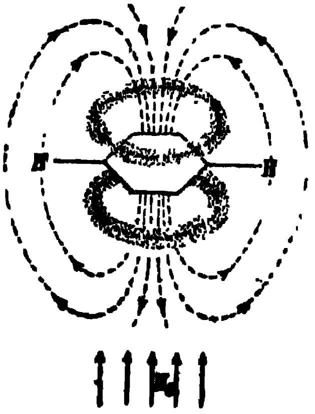


Fig. 12·26—The induced magnetic field produced by circulation of electrons around the proton of σ bond of a C—H bond opposes the applied magnetic field and thus shields the proton.

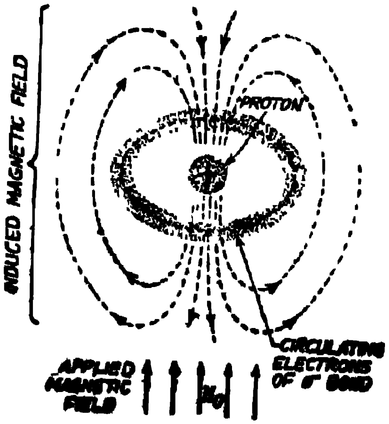


Fig. 12·27—The induced magnetic field of the π electrons of benzene nucleus reinforces the applied magnetic field and thus deshields the benzene protons.

As a result of shielding and deshielding the position of the *pmr* signal shifts from the position it would have had if there were no shielding or deshielding. As these shifts are caused by the circulation of electrons in chemical bonds, these are termed ***chemical shifts.***

Chemical shifts are measured with reference to *pmr* signal of some standard compound. The standard compound used for the purpose is tetramethylsilane (TMS). A small quantity of TMS is added to the sample while getting its *pmr* spectrum. Several reasons why TMS is used as a reference compound are :

(i) It has 12 equivalent protons which give an intense single signal. Therefore, even a small quantity of it gives a measurable signal.

(ii) Silicon is less electronegative than carbon, protons of TMS are, therefore, highly shielded. They give a *pmr* signal in a region where few other protons absorb. Hence signal of the reference compound seldom interferes with the signals from other protons.

(iii) It is inert and volatile. It can, therefore, be easily removed by evaporation after the experiment is over.

Chemical shifts are measured in Hertz (cycles per second, cps), on the assumption that the frequency of electromagnetic radiation is being varied whereas in actual practice magnetic field is changed. The two, however, being mathematically related, this amounts to the same thing.

Magnitude of chemical shifts in Hertz is proportional to the strength of the applied magnetic field. In view of the fact that different *pmr* spectrometers use different magnetic fields (usually 40, 60 or 100 Mcps), it has been considered desirable that chemical shifts be expressed in the form which is independent of the strength of the applied field.

To achieve this end, these are expressed as a fraction of the total field multiplied by 10^6 and reported as parts per million (ppm).

For example a *pmr* signal comes at 80 cps downfield with reference to TMS in a spectrometer using 40 Mcps.

$$\text{Chemical shift} = \frac{80 \times 10^6}{40 \times 10^6} = 2{\cdot}00 \text{ ppm}$$

In another instrument using 60 Mcps, the same signal will be 120 cps downfield. Its

$$\text{Chemical shift} = \frac{120 \times 10^6}{60 \times 10^6} = 2{\cdot}00 \text{ p/m}$$

This shows that ppm units are dimensionless and independent of the radiofrequency and the magnetic field employed in the *pmr* spectrometer. Further, numerator is multiplied by 10^6 only to avoid fractional values of ppm.

Two scales employed to express chemical shifts in terms of ppm are :

(i) **The δ (delta) scale, wherein**

$$\delta = \frac{\Delta\nu \text{ (in cps)} \times 10^6}{\text{Radiofrequency used (in Mcps)} \times 10^6}$$

(ii) **The τ (tau) scale, wherein $\tau = 10 - \delta$**

On the δ scale, position of TMS signal is taken 0·0 ppm whereas on τ scale it is assigned the value 10·0 ppm. Most chemical shifts on the δ scale have values between 0 and -10 and on τ scale between 0 and 10.

Values of proton chemical shifts for some common groups containing hydrogen are given in Table *12·4*.

Example 12·10. *An organic compound X gives two pmr signals at 75 cps and 300 cps using radiofrequency of 90 Mcps. Calculate their relative positions if the radiofrequency used were 60 Mcps and express the same in δ scale and τ scale.*

Solution.

Calculation of chemical shift at radiofrequency 60 Mcps.

Since the chemical shift is directly proportional to the radiofrequency, as the radiofrequency decreases from 90 Mcps to 60 Mcps, chemical shift will decrease from 75 cps to

$$\frac{75 \times 60}{90} = 50 \text{ cps}$$

Similarly, as the radiofrequency decreases from 90 Mcps to 60 Mcps, chemical shift will decrease from 300 cps to

$$\frac{300 \times 60}{90} = 200 \text{ cps}$$

Expressing the chemical shift in δ and τ scales :

Signal at 50 cps in a 60 Mcps spectrometer will have

$$\delta = \frac{\Delta\nu \text{ (in cps)} \times 10^6}{\text{RF (in Mcps)} \times 10^6} = \frac{50 \times 10^6}{60 \times 10^6} = 0{\cdot}88$$

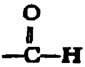
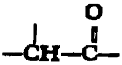
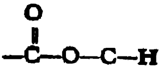
and $$\tau = 10 - \delta = 10 - 0{\cdot}88 = 9{\cdot}12$$

Similarly for signal at 200 cps in a 60 Mcps spectrometer

$$\delta = \frac{200 \times 10^6}{60 \times 10^6} = 3{\cdot}33$$

and $$\tau = 10 - 3{\cdot}33 = 6{\cdot}67.$$

Table 12·4—Typical Proton Chemical Shifts.

Type of Proton	*Chemical Shifts ppm*	
	δ	τ
Primary $R—CH_3$	0·9	9·1
Secondary R_2CH_2	1·3	8·7
Tertiary R_3CH	1·5	8·5
Vinylic $>C=CH_2$	4·6—5·9	4·1—5·4
Acetylenic $—C\equiv CH$	2—3	7—8
Aromatic Ar—H	6—8·5	1·5—4
Benzylic $Ar—CH_3$	2—3	7—8
Allylic $>C=\overset{\mid}{C}—CH_3$	1·7—1·8	8·2—8·3
Alkyl fluoride $>CH—F$	4—4·5	5·5—6
Alkyl chloride $>CH—Cl$	3—4	6—7
Alkyl bromide $>CH—Br$	2·7—4	6—7·3
Alkyl iodide $>CH—I$	2—4	6—8
Alcohols $>CH—OH$	3·4—4	6—6·6
Ethers $R—O—CH<$	3·3—4	6—6·7
Aldehydes  $—\overset{O}{\overset{\|}{C}}—H$	9—10	0—1
Ketones  $—\overset{\mid}{C}H—\overset{O}{\overset{\|}{C}}—$	2—2·7	7·3—8
Esters  $—\overset{O}{\overset{\|}{C}}—O—C—H$	2—2·2	7·8—8
Hydroxylic* $R—OH$	1—6	4—9
Phenolic* $Ar—OH$	4—12	(−2)—6
Amino* $R—NH_2$	1—5	5—9
Carboxylic* $R—COOH$	10—12	(−2)—0

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*For these groups the chemical shift varies with temperature, concentration and nature of solvent.

23. Number of Peaks in the PMR Spectra and the Number of Equivalent Protons.—Fig. 12·28 shows the pmr spectrum of *p*-xylene in which magnetic field strength is given along the abscissa in cps as well as on a delta scale in units of ppm. A small signal at $\delta=0$ is the one given by the standard TMS. Two signals at $\delta=7$ ppm and $\delta=2$ ppm show the presence of two kinds of protons (6 methyl and 4 nuclear).

Thus the number of peaks in a pmr spectrum gives the kinds of equivalent protons in the compound.

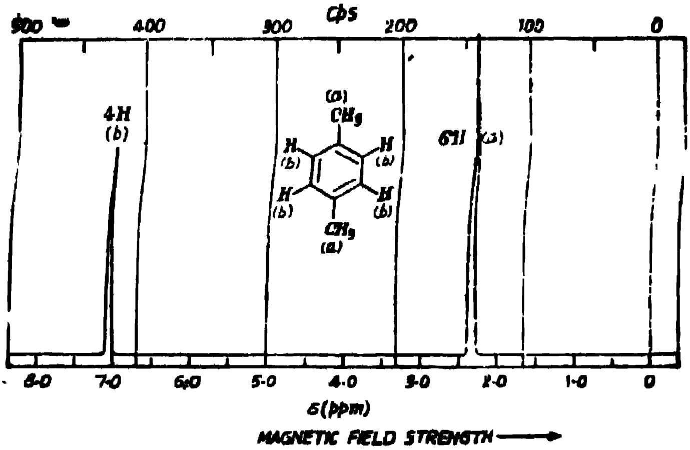


Fig. 12·28—PMR spectra of *p*-xylene.

24. Peak Area and Proton Counting.—Number of signals in a pmr spectrum gives the number of sets of equivalent protons and their positions give a clue to the types of protons. Another useful aspect of pmr spectrum is the relative intensities of these signals, indicated by the areas under various absorption peaks. *The intensity of a signal is directly proportional to the number of equivalent protons giving that signal.* Ratio between the areas under different peaks, therefore, gives the ratio between the number of different types of protons. For example, in pmr spectrum of *p*-xylene (Fig. 12·28), two signals indicate the two types of protons (6 methyl protons and 4 ring protons). Signal from methyl protons is bigger than the one from nuclear protons. Areas under these peaks have been found to be in the ratio 3 : 2 which is actually the ratio between the methyl protons (=6) and ring protons (=4).

25. Splitting of Signals : Spin-Spin Coupling.—In the pmr spectrum of *p*-xylene (Fig. 12·28), there are two signals each consisting of single peak. Spectrum of $CHCl_2—CH_2Cl$, 1, 1, 2-trichloroethane (Fig. 12·29) is somewhat different. In this there are two signals, one of which is split into two peaks and the second is split into three peaks.

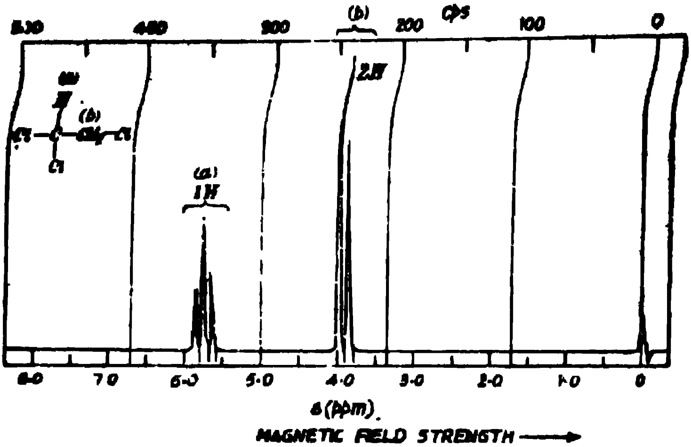


Fig. 12·29—PMR spectrum of 1, 1, 2-trichloroethane.

Signal splitting is caused by the magnetic influences of hydrogens on adjacent atoms. For example signal (*b*) from two equivalent protons of —CH_2Cl group is split into two peaks (a doublet) under the magnetic influence of the non-equivalent proton of the neighbouring hydrogen in the $CHCl_2$ group. Similarly signal (*a*) from the hydrogen of the —$CHCl_2$ group is split into three peaks (a triplet) under the magnetic influences of the two equivalent protons of the neighbouring —CH_2Cl group. This can be explained as being due to spin-spin coupling of the absorbing and the neighbouring protons.

Spin-spin splitting is observed only when non-equivalent proton is present in the neighbourhood. Thus no signal splitting is observed in the signal from six equivalent protons of ethane.

CH_3—CH_3 (*No signal splitting*)

Let us consider a molecule with two non-equivalent hydrogens H_a and H_b. In the absence of H_b, we shall get one signal from H_a. In the presence of H_b, we shall observe signal splitting. Let us see, how ?

Proton of the neighbouring hydrogen H_b can have two possible orientations :

(*i*) It may be aligned with the applied magnetic field H_0. In this case the small magnetic moment of H_b adds to the large applied field, H_0. Hence the proton of H_a experiences a magnetic field which is a sum of these two and absorbs energy at a slightly lower applied field strength (downfield) than it would have done the absence of H_b.

(*ii*) It may be aligned against the applied magnetic field H_0. In this case the small magnetic moments of H_b oppose the large applied field, H_0. Hence the proton of H_a experiences a magnetic field=difference of these two and absorbs energy at a slightly higher applied field strength (upfield), *than it would have done if H_b were not present.*

Now it can be reasonably assumed that at any time probabilities of alignment with and against the applied field are equal. In other words, protons in roughly half the molecules of H_b are aligned with the magnetic field and the remaining half are aligned against the applied magnetic field. The signal H_a is, therefore, split into two peaks of roughly equal intensity termed as *a 1 : 1 doublet.*

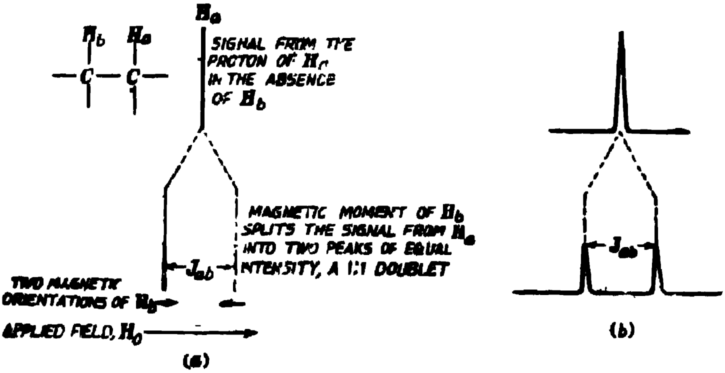

H_b
H_a
C
C
H_a
SIGNAL FROM THE PROTON OF H_a IN THE ABSENCE OF H_b
MAGNETIC MOMENT OF H_b SPLITS THE SIGNAL FROM H_a INTO TWO PEAKS OF EQUAL INTENSITY, A 1:1 DOUBLET
J_{ab}
TWO MAGNETIC ORIENTATIONS OF H_b
APPLIED FIELD, H_0
(a)
J_{ab}
(b)

Fig. 12'30—Signal splitting resulting from spin-spin coupling with one non-equivalent proton of a neighbouring hydrogen atom. Actual appearance of the spectrum after splitting is as shown in (*b*).

The distance between the two centres of peaks of the 1 : 1 doublet is termed Coupling constant J_{ab} measured in hertz. J_{ab} is independent of the magnitude of the applied magnetic field and operating frequency of the spectrometer used.

As discussed above one non-equivalent proton (H_b) on an adjacent carbon splits the signal of an absorbing proton (H_a) into a 1 : 1 doublet. Two equivalent protons (H_b) on an adjacent carbon (or two adjacent carbons) split the signal from an absorbing proton (H_a) into three peaks (*a triplet*).

Both the neighbouring protons (H_b) may be aligned with the applied magnetic field, H_0 and thereby add their tiny magnetic field to H_0. As a result proton absorbs energy at a lower field strength (downfield) than would have done in the absence of the two hydrogen atoms (H_b).

Alternatively, the two protons (H_b) may be aligned against the applied magnetic field, Ho and thus lower the strength of the applied magnetic field. As a result the proton (H_a) absorbs energy at a slightly higher applied field strength (upfield) than it would have done in the absence of the two H_b hydrogen atoms.

In addition to these, two more alignments are possible ; in each of these one opposes the other. In both cases one reinforces the applied field while the other opposes it. Their effects cancel each other and the applied field remains unchanged. Thus the signal is not displaced at all.

Since the probability of the last arrangement is double than that of the first or second, the central peak of the triplet is twice as intense and it is termed 1 : 2 : 1 *triplet.*

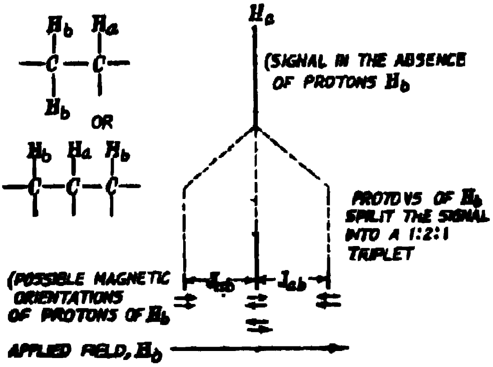
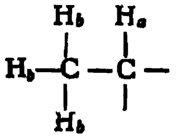

Hb Ha
—C—C—
Hb
OR
Hb Ha Hb
—C—C—C—
Ha
(SIGNAL IN THE ABSENCE OF PROTONS Hb
PROTONS OF Hb SPLIT THE SIGNAL INTO A 1:2:1 TRIPLET
Jab
Jab
(POSSIBLE MAGNETIC ORIENTATIONS OF PROTONS OF Hb
APPLIED FIELD, H0

Fig. 12·31—Two Protons marked H_b split the signal of H_a into a 1 : 2 : 1 triplet.

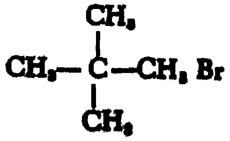
Similarly, three equivalent protons (H_b) attached to the adjacent carbon atom in



$$\begin{array}{ccc} & H_b & H_a \\ & | & | \\ H_b— & C— & C— \\ & | & | \\ & H_b & \end{array}$$

will split the signal of absorbing proton ($—H_a$) into a 1 : 3 : 3 : 1 quartet.

Rules governing Splitting of Signals. (i) *Splitting of signals is caused only by protons attached to adjacent carbon (or carbons) provided these are not equivalent to the absorbing proton.* In 1-bromo-2, 2- dimethyl propane



$$\begin{array}{ccc} & CH_3 & \\ & | & \\ CH_3— & C & —CH_2Br \\ & | & \\ & CH_3 & \end{array}$$

There is no splitting of signals since the non-equivalent protons are not attached to adjacent carbons.

(ii) *The number of peaks obtained after splitting is one more than the number of vicinal protons* (protons attached to adjacent carbon or carbons). Thus one vicinal proton gives a 1 : 1 doublet, two give a 1 : 2 : 1 triplet, three give a 1 : 3 : 3 : 1 quartet and so on.

(iii) *All the peaks of a doublet, triplet, quartet, etc., are not exactly of the same intensity. The inner peaks are always bigger than the outer ones* (*see* Fig. 12·29).

Example 12·11. *A compound having molecular formula* $C_{10}H_{14}$ *gave the following pmr data*

(*a*) *A singlet,* τ *9·12 (*δ *0·88), 9H*

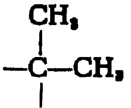
(*b*) *A singlet,* τ *2·72 (*δ *7·28), 5H*

Give a structure of the given compound consistent with the above data. (*Punjab B.Sc. II, 1976*)·

Solution.

The formula $C_{10}H_{14}$ corresponds to the general formula of an aromatic hydrocarbon. C_nH_{2n-6}.

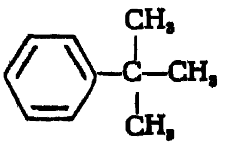
Two signals suggest that there are only two kinds of protons. The set of 5 protons may be the protons of benzene ring. This is confirmed by ppm of the signal=τ 2·72 (δ 7·28). So the given compound is some mono-substituted benzene with side chain C_4H_9 containing nine equivalent protons (second set). Alkyl group C_4H_9 with nine equivalent hydrogen atoms must be tertiary butyl group.



$$-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_3$$

This is further confirmed by the value of τ 9·12 (δ 0·88) which is due to methyl protons.

Hence the structural formula of the given compound $C_{10}H_{14}$ is



(*tert-Butylbenzene*)

Since both pmr signals are singlets, this means the two kinds of protons are not coupled. The above formula is further supported by this fact since in it there are no protons to give spin-spin coupling.

Example 12·12. *An organic compound with molecular formula $C_3H_3Cl_5$ gave the following pmr data :*

(*a*) *A triplet, τ 5·48 (δ 4·52), 1 H*

(*b*) *A doublet, τ 3·93 (δ 6·07), 2 H*

Assign a structural formula to the compound consistent with its pmr data given above. (*Punjab B.Sc. 1975*)

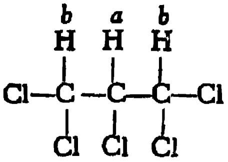
Solution.

The formula $C_3H_3Cl_5$ suggests that it is a substituted propane (some pentachloropropane). Two signals suggest that it contains two kinds of protons. Two protons giving a doublet are equivalent. Let each one of these be named H_b. Let the other proton giving a triplet be named H_a.

Signal of two equivalent H_b protons is split into a doublet by the non equivalent proton H_a as a result of spin-spin coupling.

Similarly, signal of H_a proton is split into a 1 : 2 : 1 triplet by two H_b protons.

Structural formula of $C_3H_3Cl_5$ with two equivalent H_b protons and one more proton H_a not equivalent with H_b protons can be


$$\overset{\overset{b}{H}}{\underset{Cl}{Cl-C}}-\overset{\overset{a}{H}}{\underset{Cl}{C}}-\overset{\overset{b}{H}}{\underset{Cl}{C-Cl}}$$

1, 1, 2, 3, 3-pentachloropropane

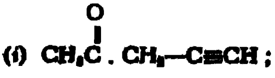
In this two protons attached to carbon atoms no. 1 and 3 are equivalent. These are, however, not equivalent with the proton attached to carbon atom No. 2.

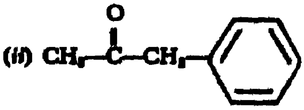
Answer the following Questions :

1. How many groups of non-equivalent protons are present in the compound $CH_2=CH-CH_2-OH$ and what is the ratio of the number of protons in each group ?

2. The compound $C_6H_5-CH\ (CH_3)-O-CH\ (CH_3)-C_6H_5$ has nmr protons signals at 2·82 τ (7·18 δ) 5·56 τ and 5·57 τ. Assign these peaks to the protons in the compound and predict the multiplicity of each peak.

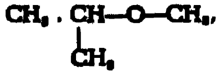
3. How many different types of nmr signals would you expect to find in the spectrum of each following compounds :

(*i*) 
$CH_3\overset{O}{\overset{\|}{C}}.\ CH_2-C\equiv CH$;

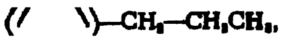
(*ii*) 

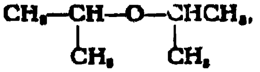
(*iii*) $CH_3\ CH_2\ CH_2\ CH_2\ CH_2\ Br$.

4. Which of the following substances could give the nmr spectrum having doublet at 1·3 ppm and a heptet at 3·8 ppm.

(i) 
$CH_3.CH(CH_3)-O-CH_3$,

(ii) $CH_3CH_2CH_2CH_3$,

(iii) 
$C_6H_5-CH_2-CH_2CH_3$,

(iv) 
$CH_3-CH(CH_3)-O-CH(CH_3)CH_3$,

(v) $CH_3CH_2OCH_2CH_3$.

5. Give a structure or structures consistent with each of the following sets of NMR.

(i) $C_3H_3Cl_5$ (a) triplet, τ 5·48 (δ 4·52), 1H (b) doublet, τ 3·93 (δ 6·07), 2H

(ii) $C_{10}H_{14}$ (a) singlet, τ 8·70 (δ 1·30), 9H (b) singlet, τ 2·72 (δ 7·28), 5H

(Punjab B.Sc. II, 1975)

6. From the following sets of pmr give a structure consistent with each of the following :

(i) $C_{10}H_{14}$: (a) singlet, τ 9·12 (δ 0·88), 9 H (b) singlet. τ 2·72 (δ 7·28), 5H

(ii) $C_{10}H_{13}Cl$: (a) singlet. τ 8·43 (δ 1·57), 6H (b) singlet, τ 6·93 (δ 3·07), 2H (c) singlet, τ 2·73 (δ 7·27), 5H

(iii) $C_9H_{11}Br$: (a) quintet, τ 7·85 (δ 2·15), 2H (b) triplet, τ 7·25 (δ 2·75), 2H (c) triplet, τ 6·62 (δ 3·38), 2H (d) singlet, τ 2·75 (δ 7·25), 5H

(Punjab B.Sc. II, 1976)

7. Draw the schematic NMR spectra of acetone and acetaldehyde. Is the separation between the peaks dependent on the applied field ?

(Delhi B.Sc. Hons. 1981)

8. How many proton signals would be expected in NMR spectra of each of the following compounds ? Indicate also the multiplicity of various signals.

(a) CH_3-O-CH_3 (b) CH_3-CH_2-OH

(c) $CH_3-O-CH_2-CH_3$ *(Delhi B.Sc. Hons. 1980)*

HINTS AND ANSWERS

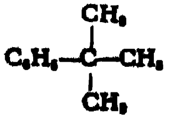
1. Five ; Ratio 1 : 1 : 1 : 2 : 1.

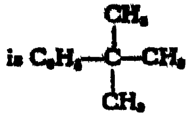
2. 2·82 τ Phenyl group, singlet.
5·56 τ methine, quartet.
8·57 τ methyl, doublet.

3. (i) 3 (ii) 3 (iii) 5.

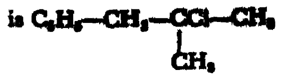
4. (iv)—diisopropyl ether gives heptet-doublet signals.

5. (i) $C_3H_3Cl_5$ is $CHCl_2.CHCl.CHCl_2$ (1, 1, 2, 3, 3-penta-chloropropane)

(ii) $C_{10}H_{14}$ is 
$C_6H_5-C(CH_3)_3$ (tert-Butylbenzene)

6. (i) is 

$C_6H_5-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$

(ii) is 

$C_6H_5-CH_2-\underset{CH_3}{CCl}-CH_3$

(iii) is $C_6H_5-CH_2-CH_2-CH_2Br$

7. For a schematic NMR spectrum of acetone draw a singlet at ppm δ 2—2·5 (6 protons).

For that of acetaldehyde draw a doublet at ppm δ 2—2·5 (3 protons) and another quartet at ppm δ 10—12 (1 proton).

8. (a) One, singlet

(b) three—triplet (for CH_3) ; quartet (for CH_2) ; singlet (for OH)

(c) three—singlet (for OCH_3) ; quartet (for CH_2) ; triplet (for CH_3)

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26. **Mass Spectrometry.** Mass spectrometry is the most accurate method for determining the molecular mass of a compound and its elemental composition. With this information, we can arrive at the molecular formula of the compound as well as the structural data.

When vapour of a compound, in high vacuum, is bombarded with a moving beam of high energy electrons (≈ 70 eV), ionization of some molecules occurs. In one form of ionization, one of the valency electrons of the molecule is knocked out resulting in the formation of a **radical cation** (a positively charged ion).

$$\text{Molecule} + e^- \rightarrow \underset{\text{Radical cation}}{(\text{Molecule})^+} + 2\,e^-$$

The positively charged ion is also called **molecular or parent ion** and designated as M^+ or P^+. It is positively charged molecule with an unpaired electron.

Energy required to knock out an electron (inonization potential) is only about 10-15 eV. Energy of the electron in practice being 50-75 eV, the molecular ion is formed with an excess of energy which is large enough to break it down into a mixture of neutral and positively charged fragments.

Each kind of ion has a particular mass to charge ratio or *m/e* value. For most ions, the charge is 1, so that *m/e* (mass to charge ratio) is simply the mass of the ion.

All positive ions are accelerated in an electric field and then passed through a magnetic field when these get separated. Ions having the same mass-to-charge ratio are, thus, collected into beams.

The set of ions is analysed in such a way that a signal is obtained for each value of *m/e*, the intensity of each signal reflects the relative abundance of the ion producing signal. The largest peak is called the base peak, its intensity is taken as 100 and the intensities of other peaks are expressed relative to it.

Mass spectra can be used in two general ways :

(a) to prove the identity of two compounds ;

(b) to establish the structure of a new compound.

Mass spectrum helps to establish the structure of a new compound in :

(i) giving an exact molecular mass.

(ii) giving a molecular formula—or at least narrow the possibilities to a few.

(iii) indicating the presence in a molecule of certain structural units.

Gases, liquids and solids may be used in determination *of mass spectra. Solvents are not normally needed or used.*

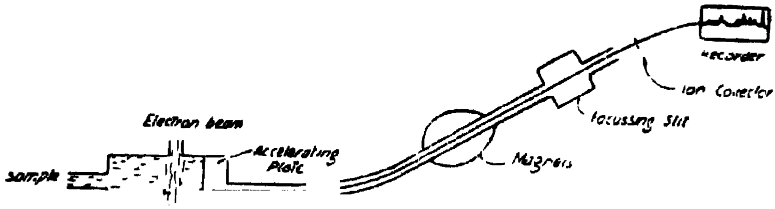


Fig. 12·32—Schematic diagram of a mass spectrometer.

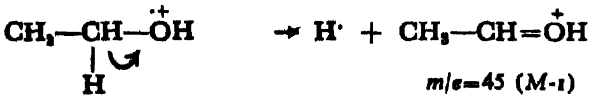
The fragmentation of organic molecules follows certain patterns which are very useful, in determining the structure of the molecule. First of all, the particles of highest mass usually correspond to the molecular mass of the original molecule. The molecular ion immediately tells the molecular mass of the compound. Secondly, the fragmentation of the molecular ion often gives carbocations of characteristic masses, *e.g.*, the bombardment of ethanol vapours by a high-energy electron beam follows the course shown below :

$$CH_3—CH_2—\overset{\cdot\cdot}{O}H + e^- \rightarrow CH_3—CH_2—\overset{\cdot +}{O}H + 2e^-$$

$$m/e=46\ (M^+)$$

$$\rightarrow CH_3\,. + CH_2=\overset{+}{O}H$$

$$m/e=31\ (M\text{-}15)$$



$$\underset{\displaystyle H}{\underset{|}{CH_3—CH}}—\overset{\cdot +}{O}H \rightarrow H^\cdot + CH_3—CH=\overset{+}{O}H$$

$$m/e=45\ (M\text{-}1)$$

$$CH_3—CH_2—OH + e^- \rightarrow [CH_3—CH_2—OH]^{\overset{+}{\cdot}} + 2e^-(M^+)$$

$$[CH_3—CH_2—OH]^{\overset{+}{\cdot}} \rightarrow HO^\cdot + CH_3—\overset{\cdot\cdot}{C}H_2$$

$$m/e=29\ (M\text{-}17)$$

Only a few of the many possible decomposition paths have been given above.

Mass spectrum of ethanol is shown in Fig. 12·33. It shows only the most intense lines.

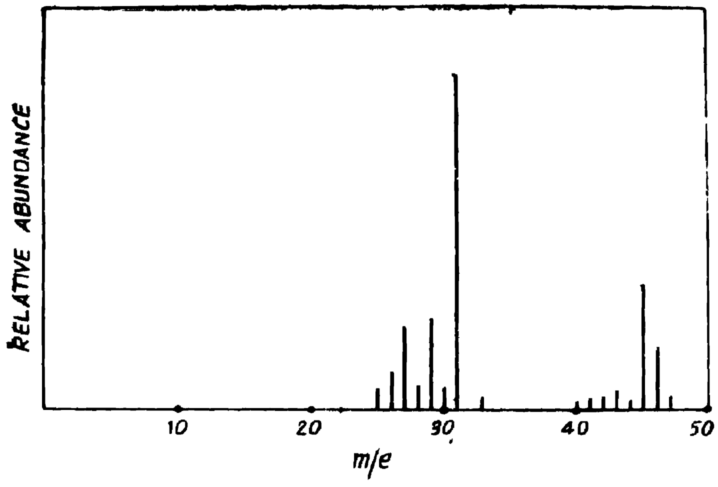


Fig. 12·33—Mass spectrum of ethanol.

QUESTIONS

1. What is the principle underlying mass spectroscopy ?
2. To what uses are the mass spectra put ?

Appendix

NEW TYPE QUESTION BANK—I

1. What is the purpose of :

(*a*) adding one or two porcelain pieces during distillation of a liquid ?

(*b*) taking glass beads in fractionating column in fractional distillation ?

(*c*) recommending slow heating in case of sublimation or in the determination of melting/boiling point of an organic compound ?

(*d*) the addition of $CuSO_4$ and K_2SO_4 during kjeldahlising ?

(*e*) use of sodium metal in Lassaigne's test ?

(*f*) boiling with conc. HNO_3 while testing for halogens ?

(*g*) platinum chloride in the determination of molecular weights of bases ?

(*h*) $AgNO_3$ in the determination of molecular weights of acids ?

(*i*) oxidised copper spiral in the combustion tube in estimation of carbon and hydrogen in organic compounds ?

(*j*) vacuum desiccator in the purification of organic compounds ?

(*k*) determination of melting/boiling point of organic compounds ?

2. (*a*) What is the principle underlying chromatography ?

(*b*) Name the fixed phase and the stationary phase in the following :

(i) Column chromatography. (ii) Thin layer chromatography
(iii) Partition chromatography. (iv) Gas chromatography.

(*c*) What is R_F value ?

(*d*) What is a gas chromatogram ?

3. What is the principle underlying zone refining ?

4. What is the use of mixed melting point in identification of organic compounds ?

5. Name various quantum numbers. Write their possible values for an electron in the M shell.

6. State Pauli's exclusion principle. How many electrons can there be in the following orbitals ?

(*i*) 1 *s*, (*ii*) 1 *p*, (*iii*) 2 *s*, (*iv*) 2 *p*, (*v*) 2 *d*,
(*vi*) 3 *s*, (*vii*) 3 *p*, (*viii*) 3 *d*, (*ix*) 3 *f*, (*x*) 4 *s*,
(*xi*) 4 *p*, (*xii*) 4 *d*, (*xiii*) 4 *f*.

7. What is aufbau principle ?

8. State the working rule for deciding which one of the two given orbitals is of lower energy

9. Arrange the following orbitals in the order of increasing energy : 3*s*, 3*p*, 3*d*, 4*s*, 4*p*, 4*d*, 4*f*, 5*s*, 5*p*

10. What is the physical significance of ψ and ψ^2 ?

11 How does electronegativity of an atom affect the polarity of bond it forms ?

12. Which of the following compounds do you expect to be ionic ? Give the electron dot structures for each.

(i) NaBr, (*ii*) $MgCl_2$, (*iii*) PH_3, (*iv*) NF_3,
(*v*) S_2Cl_4, (*vi*) H_2S, (*vii*) CH_2Cl_2, (*viii*) CH_3OH,
(*ix*) CCl_4, (*x*) CO_2, (*xi*) HCN, (*xii*) H_2O_2.

13. What is dipole moment ? How does it vary with electronegativity difference between the constituent atoms ? In what units is dipole moment expressed ?

14. Indicate the direction of the dipole moment, if any, in the following compounds :

(i) HF, (*ii*) CH_2Cl_2, (*iii*) $CHCl_3$, (*iv*) CCl_4, (*v*) Br_2
(*vi*) CH_3OH, (*vii*) H_2O, (*viii*) NH_3 (*ix*) $(CH_3)_3N$, (*x*) ICl.

15. Dipole moments of HCl and HF are 1·63 D and 1·75 D respectively. How do you account for the difference ?

16. How can you account for the following ?

(*i*) CCl_4 has no dipole moment but $CHCl_3$ has

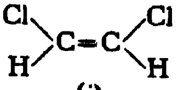
(*ii*) BF_3 has no dipole moment but NF_3 has.

(*iii*) CO_2 has no dipole moment but SO_2 has.

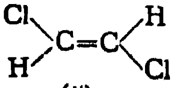
(*iv*) Dipole moment of NF_3 is 0·24 D while that of NH_3 is 1·46 D.

(*v*) PF_5 has no dipole moment but IF_5 has.

17. How can you distinguish between the following on the basis of dipole moment ?



and



(i) (ii)

18. (*a*) What is the first condition for the formation of covalent bond between two atoms ?

(*b*) What is a sigma bond orbital or localised molecular orbital ?

(*c*) What is the nature of spin of the two electrons occupying an orbital ?

(d) How do you account for the bonding force between two atoms joined by covalent bond ?

(*e*) How is strength of a covalent bond related to the extent of overlapping of two orbitals ?

(*f*) Out of *s* and *p* orbitals which will form a stronger bond and why ?

19. What are the sigma and pi bonds ?

20. Give the orbital electron representation of the following :

(i) Carbon atom (*ground state* and *excited state*) ;

(ii) Nitrogen atom ; (iii) Oxygen atom

21. Write structure of one organic compound in each of the following :

(*i*) containing an *sp* hybridised carbon.

(*ii*) containing a π bond.

(*iii*) containing all sigma bonds.

(*iv*) in which all atoms lie in the same plane.

(*v*) in which all atoms lie in a straight line.

22. Draw orbital diagrams for the following molecules :

$$CO_2, \ CO, \ H-C\equiv N$$

23. Is an *s* orbital directional ?

24. Define the following :

(*a*) Bond length, (*b*) Bond energy, (*c*) Bond angle.

25. What is the difference between dissociation energy and bond energy ?

26. What is a hydrogen bond ? Give names of three compounds showing hydrogen bonding.

27. Hydrogen bonding is important only when both electronegative atoms come from the group : F, O, N. Explain why ?

28. Explain why—

(*a*) Glycerine is far more viscous than ethanol.

(*b*) Hydrogen sulphide is a gas whereas water is a liquid.

(*c*) Methanol is quite soluble in water while carbon tetrachloride is insoluble in it.

29. Melting point of NaCl is much higher than that of $AlCl_3$. Explain why ?

30. What is an acid according to

(i) Bronsted-Lowry definition, (ii) Lewis definition ?

31. What is a Bronsted-Lowry base and a Lewis base ?

32. What are conjugate acid and conjugate base ?

33. What is the relation between the strength of an acid and its conjugate base ?

34. Knowing K_a values of two acids, how will you tell which is stronger acid ?

35. Knowing pK_a values of two acids how will you tell which is stronger acid ?

37. *Name the type of orbital used for bonding in the central atom of each of the following and predict the geometrical configuration for each :*

(*a*) NH_3 (*b*) CH_4 (*c*) NH_4^+ (*d*) H_2O (*e*) H_2S (*f*) BF_4^-

38. The order of bond lengths in the halogen acids is : $HF < HCl < HBr < HI$: the order of their dipole moments is : $HF > HCl > HBr > HI$. Offer an explanation.

39. C—O and B—F bonds are known to be polar. How will you account for the zero dipole moment of CO_2 and BF_3 ?

40. Predict the relative acidity of—

(*a*) methanol (CH_3OH) and methylamine (CH_3NH_2)

(*b*) methanol and methanethiol (CH_3SH)

(*c*) H_3O^+ and NH_4^+.

41. Which is the stronger acid of each pair :

(*a*) H_3O^+ or H_2O, (*b*) NH_4^+ or NH_3,

(*c*) H_2S or HS^-, (*d*) H_2O or I^- ?

(*e*) What relationship is there between *charge* and *activity* ?

42. Arrange the members in the following groups in the order of basicity

(*a*) F^-, Cl^-, NH_2^-, CH^-, (*b*) HF, H_2O, NH_3,

(*c*) OH^-, SH^-, SeH^-, (*d*) F^-, Cl^-, Br^-, I^-,

(*e*) H_2S, HS^-, S^{-2}, (*f*) H_3O^+, H_2O, OH^-,

(*g*) NH_3, NH_2^-, (*h*) CH_3OH, CH_3NH_2, CH_3F

43. What is Bronsted-Lowry acid in :

(*a*) HCl dissolved in water.

(*b*) HCl (unionized) dissolved in benzene ?

(*c*) Which solution is more strongly acidic ?

44. Write a short note on : Effectiveness of overlap.

45. What are the forces acting to hold the following molecules together in the liquid phase :

(*i*) Nitrogen molecules,

(*ii*) Water molecules, and

(*iii*) Sodium chloride molecules ?

46. What do you understand by the term 'resonance'? Give two examples.

47. Arrange the following in the order of decreasing basic strength :

$(CH_3)_2CH\bar{O}$, $CH_3\bar{O}$, $(CH_3)_3\bar{O}$, $H\bar{O}$

48. Indicate the difference between inductive effect and electromeric effect *giving one example in each case.*

49. Why is ethylene a planar molecule and acetylene a linear molecule ?

50. How do the bond length and bond strength vary in the following case : C—H, C—C, C=C, C≡C, C—Cl

51. Classify the following as Lewis acids or bases giving reason for your answer : diethyl ether, bisulphate anion.

52. What shapes are associated with the *sp*, sp^2 and sp^3 hybrid orbitals ?

53. On the basis of the concept of hybridization of atomic orbitals, predict the shapes of BeF_2 and BF_3 molecules.

54. The bond angles in NH_3, H_2O and CH_4 are 107°, 104·5° and 109·5° respectively. How can these values be justified if sp^3 orbitals are involved in each case ?

55. Arrange the following acids according to increasing acid strength, giving reasons for your answer : Isobutyric acid, propionic acid, α-chloropropionic acid, β chloropropionic acid.

56. How do bond length and bond strength vary in following cases : C—C, C=C, C—Cl ?

57. Write down the canonical forms of the following structures :

(*i*) $H_2N—CH=CH—CH=CH_2$ (*ii*) $H_2C=CH—CH=O$.

58. Write down :

(*i*) The conjugate base of nitromethane,

(*ii*) The conjugate acid of isopropyl alcohol.

59 Write down the different canonical forms of (*i*) acetamide, (*ii*) methyl vinyl ketone.

60. The dipole moment of CO_2 is zero and that of diethyl ether is 1·12D. Predict the shape of these molecules and indicate the direction of the dipole moments in each case.

61. Carbon-carbon double bond is shorter than carbon-carbon single bond. Explain why.

62. Carbon-carbon bond distance in benzene is intermediate between the bond distances in ethylene and ethane. Account for this.

63. Write down the electronic structure of formaldehyde and indicate the "σ electrons", "π electrons" and "n-electrons (*i.e.*, non-bonded electrons)" in it.

64. Classify giving suitable explanation, the following compounds as Lewis acids, Lewis bases, neither or both :

(i) $AlCl_3$, (ii) BF_3, (iii) NH_3 (iv) C_6H_6, (v) H_2O, (vi) C_2H_5ONa.

65. Arrange the following in the ascending order of :

(a) *Acidity* : $HClO_3$, $HClO$, $HClO_2$, $HClO_4$

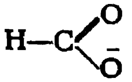
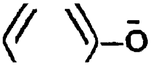
(b) *Basicity* : (i) CH_3OH, HOH, $NaOH$, $B(OH)_3$

(ii) CH_3OH, NH_3, $(CH_3)_2NH$, $(CH_3)_2O$, CH_3NH_2

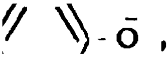
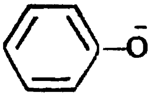
(iii) F^-, Cl^-, Br^-, I^-

(c) *Polarity* : CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4.

66. Draw resonance structures for the following :

HCO_3^-, CO_3^{2-}, NO_3^-,

, C_6H_6,


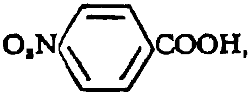
67. In the given pairs which of the two would be more stable ?

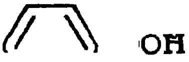
(a) I^-, Cl^- ; (b)

,


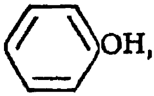
(c) $CH_3-CH_2-\overset{\oplus}{C}H_2$, $CH_2=CH-\overset{\oplus}{C}H_2$

68. Which of the following would you expect to be

(a) *Stronger acid* : (i) CH_3COOH, $ClCH_2COOH$:

(ii)




(iii)


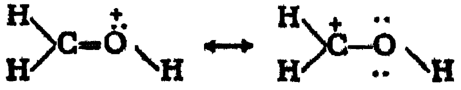
(b) *Stronger base* : (i) $C_6H_5NH_2$,

69. Which is stronger effect in the following, inductive effect or hyperconjugative effect ?

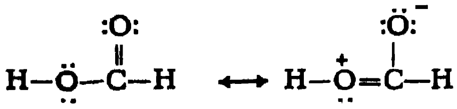
(i) $CH_2=CH-CH_2-Br$; (ii) $CH_2=CH-CH_2-OH$

70. What is responsible for the following fact : *the greater the number of alkyl groups attached to the doubly bonded carbon atoms, the more stable the alkene.*

71. Which is more stable of the two alternative resonance stabilised structures in each pair ?

(a)


(b)



$$H-\ddot{\underset{\cdot\cdot}{O}}-\overset{\overset{:O:}{\|}}{C}-H \longleftrightarrow H-\overset{+}{\underset{\cdot\cdot}{O}}=\overset{\overset{:\ddot{O}:^{-}}{|}}{C}-H$$

72. What effect does resonance have on the following ions with respect to (*a*) charge distribution, (*b*) bond distance, and (*c*) stability ?

(i) Nitrate ion, (*ii*) Carbonate ion

73. Write the formulae for the conjugate acid and conjugate base for the following :

(*a*) CH_3OH, (*b*) water, (*c*) ammonia,

(*d*) Aniline, (*e*) HCO_3^-, (*f*) $H_2PO_4^-$

74. The term autoprotolysis means self-ionisation by proton transfer, *e.g.*,

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

Write autoprotolysis reactions for the following :

(*a*) HCOOH, (*b*) CH_3OH, (*c*) H_2SO_4,

(*d*) CH_3NH_2, (*f*) NH_3.

75. Write IUPAC names for the various compounds represented by the following molecular formulae. Write their structural formulae :

(*a*) C_4H_8 ; (*b*) $C_4H_{10}O$

76. Give structural formulae of

(*i*) Methoxyethane, (*ii*) 2-Butyne,

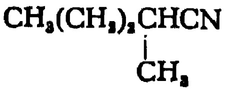
(*iii*) 2-Methyl-1-butanol, (*iv*) 2-Methyl-3-pentanone

77. Give the acceptable names for :

(*a*) CCl_3COOH, (*b*) $HOCH_2COOH$

(*c*) $CH_3C(COOH)(CH_2COOH)_2$

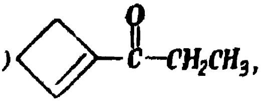
(*d*)



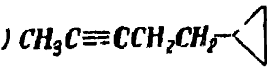
$$CH_3(CH_2)_2\underset{\underset{CH_3}{|}}{C}HCN$$

(*e*) $OHC(CH_2)_4CH(CHO)_2$

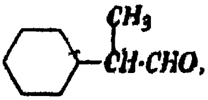
f)



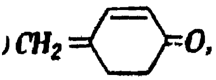
(g)



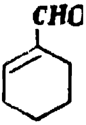
h)



(i)



(j)



78. Are the following names correct in the IUPAC system?

(*a*) 3-Pentyne, (*b*) Octanediol

(*c*) 1, 6-hexadiene, (*d*) *tert*-butanol

(*e*) 3, 4, 4-trimethyl-1-hexyne (*f*) 2-keto-*n*-propanol.

79. Write structural formulae of the following :

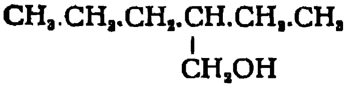
(*i*) 4-hydroxy-3-pentenoic acid,

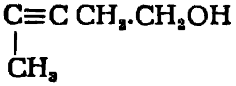
(*ii*) 6-ethyl-2-methyl-4-isopropyloct-2-ene

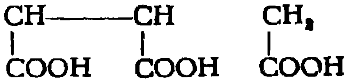
(*iii*) 1, 5-hexadiene

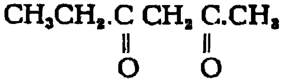
(*iv*) 4-Methyl-2-pentyne.

80. Write IUPAC names for the following :

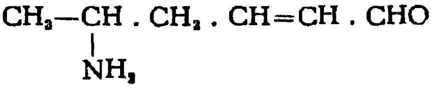
(*i*)

$CH_3.CH_2.CH_2.\underset{\overset{|}{CH_2OH}}{CH}.CH_2.CH_3$

(*ii*)

$\underset{\overset{|}{CH_3}}{C}\equiv C\;CH_2.CH_2OH$

(*iii*)

$\underset{\overset{|}{COOH}}{CH}——\underset{\overset{|}{COOH}}{CH}\qquad\underset{\overset{|}{COOH}}{CH_2}$

(*iv*)

$CH_3CH_2.\underset{\overset{\|}{O}}{C}\;CH_2\;\underset{\overset{\|}{O}}{C}.CH_3$

(*v*) $(CH_3)_2CH—CH=CH—C\equiv CH$

(*vi*)

$CH_3—\underset{\overset{|}{NH_2}}{CH}\;.\;CH_2\;.\;CH=CH\;.\;CHO$

81. Define isomerism. Name five types of structural isomerism giving one example of each.

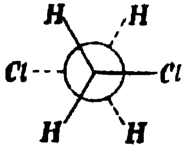
82. What is the difference between tautomerism and resonance ?

83. Which of the following would show geometrical isomerism ?

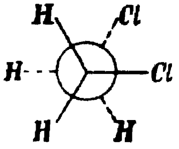
(*a*) 2-Butene, (*b*) 1-Pentene, (*c*) 2-Pentene,

(*d*) 4-ethyl-2 methyl -3-hexene (*e*) 2-Methyl-2-butene.

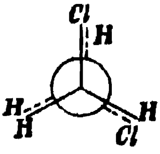
84. Name the conformation of each of the following formulae:



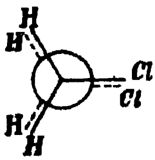
(i)



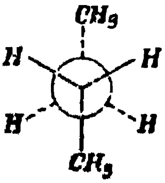
(ii)



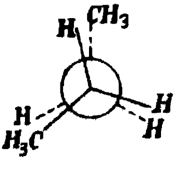
(iii)



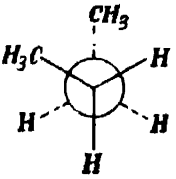
(iv)



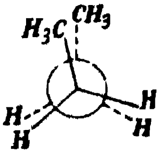
(v)



(vi)



(vii)



(viii)

85. Judge whether the following IUPAC names are correct :
(*a*) 2-ethylbutane (*c*) 2, 3-dimethylbutane
(*c*) 3-dimethylpentane (*d*) 1-bromoethanoic acid
(*e*) diethylaminobenzene.

86. Illustrate, with formulae, the difference in the use of terms primary, secondary and tertiary,

(*a*) as applied to classes of amines and as applied in names of amines, (*b*) as applied to alcohols.

87. In how many stereo-isomers can

HOOC—CHOH—CHOH—COOH exist ?

88. Lactic acid exhibits optical isomerism whereas propionic acid does not. Explain why ?

89. How will you differentiate between Enantiomers and Diastereoisomers ?

90. What is the difference between configuration and conformation ?

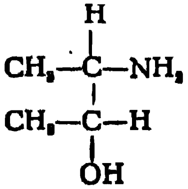
91. What is the difference between racemic and meso form ?

92. Different conformers of dichloroethane cannot be isolated. Explain why ?

93. What is polarised light ?

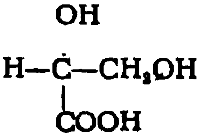
94. What is the requirement of a compound to show optical activity ?

95. Give the absolute configuration at each of the chiral carbon atoms in the following two compounds :



$$\mathrm{CH_3-\underset{\underset{CH_3-\underset{\underset{OH}{|}}{C}-H}{|}}{\overset{\overset{H}{|}}{C}}-NH_2}$$

and



$$\mathrm{H-\underset{\underset{COOH}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2OH}$$

96. Out of chair and boat conformation of cyclohexane, which one is more stable and why ?

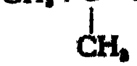
97. How many isomers of 2-iodobutane are possible ? Why ? (*Madras B.Sc. 1976*)

98. 0·38 g of the silver salt of an organic dibasic acid on ignition gave 0·216 g of silver. Find the molecular weight of the acid. (*Madras B.Sc., 1976*)

99. Write down the possible structures of the compound C_4H_9Cl and name them. (*Madras B.Sc. 1976*)

100. Suggest explanations of the following reactions :

(*a*) Isobutane $\xrightarrow{Br_2/light}$ t-butyl bromide

(*b*) 

$\mathrm{CH_3\,.\,\underset{\underset{CH_3}{|}}{C}=CH_2} \xrightarrow{HCl}$ t-butyl chloride

(*Madras B.Sc. 1976*)

101. What is the physical significance of a wave function ? *(Madras B.Sc. 1977)*

102. State the Pauli exclusion principle. *(Madras B.Sc. 1977)*

103. What is the function of magnetic quantum number in describing structure of an atom ? *(Madras B.Sc. 1977)*

104. Correct the errors in the nomenclature of the following :

(*i*) 3,3,6-Trimethyl-5-ethylheptane.

(*ii*) 2-Ethylpropane.

(*iii*) 2, 4, 4-Trimethyl-3-ethylpentane. *(Madurai B.Sc. 1976)*

105. Grade the following in the order of decreasing acid strength. Give reasons.

(*a*) HF, HCl, HBr and HI.

(*b*) HOCl, $HClO_2$, $HClO_3$ and $HClO_4$. *(Calicut B.Sc. 1978)*

106. Give suitable explanation for the following :

(*i*) 2-Butanol on dehydration gives 2-Butene.

(*ii*) *tert.* Alkyl halides usually react by S_N1 mechanism. *(Delhi B.Sc. Hons. 1978)*

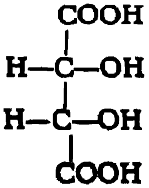
107. How will you define an acid in terms of (i) Bronsted-Lowry and (ii) Lewis concepts ? Give suitable examples. *(Delhi B.Sc. Hons. 1978)*

108. Give reasons and state which is the stronger acid in each of the following pairs :

(*i*) H_3O^+ or H_2O ; (*ii*) NH_4^+ or NH_3 ;
(*iii*) H_2S or HS^- ; (*iv*) H_2O or OH^- ? *(Delhi B.Sc. Hons. 1978)*

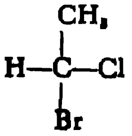
109. Label the following with R and S notations :

(*i*)



$$\begin{array}{c} COOH \\ | \\ H-C-OH \\ | \\ H-C-OH \\ | \\ COOH \end{array}$$

(*ii*)



$$\begin{array}{c} CH_3 \\ | \\ H-C-Cl \\ | \\ Br \end{array}$$

(Delhi B.Sc. Hons. 1978)

Objective Type Questions :

Select the correct answer :

1. A carbocation rearranges itself to give a more stable carbocation. In this rearrangement the migrating atom or group leaves as

(*a*) a free radical, (*b*) a positively charged ion,
(*c*) a negatively charged ion.

2. Which of the following is an electrophile ?

(*a*) $AlCl_4^-$, (*b*) BCl_3, (*c*) NH_3, (*d*) CH_3OH,

3. A nucleophile must necessarily have

(*a*) an unpaired electron. (*b*) a lone pair of electrons.
(*c*) an overall positive charge. (*d*) an overall negative charge.

4. Which of the following statements does not apply to a free radical chain reaction :

(*a*) It may be initiated by ultraviolet light.

(*b*) One mole of product is obtained for each mole of free radicals produced in the initiation step.

(*c*) It is not affected by changes in polarity of the solvent.

(*d*) It is inhibited by the presence of certain substances.

5. Main product obtained when propene reacts with chlorine at 725K is :

(*a*) $CH_3.CHCl.CH_2Cl$ (*b*) $CH_2Cl.CHCl.CH_2Cl$

(*c*) $CH_2Cl.CH=CH_2$ (*d*) $CHCl=CCl.CH_3$

6. In the dehydration reaction given below the hybridisation state of carbon atom changes from :

$$CH_3CONH_2 \xrightarrow{P_4O_{10}} CH_3.C{\equiv}N$$

(*a*) sp^2 to sp^3, (*b*) sp to sp^3,

(*c*) sp^2 to sp, (*d*) sp to sp^2.

7. Most stable carbocation obtained as an intermediate product during dehydration of 1-butanol ($CH_3.CH_2.CH_2CH_2OH$) is :

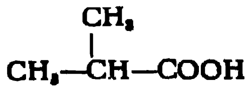
(*a*) $CH_3.CH_2.CH_2.\overset{\oplus}{C}H_2$, (*b*) $CH_3.CH_2.\overset{\oplus}{C}H.CH_3$,

(*c*) $CH_3.CH_2.\overset{\oplus}{C}H_2\ CH_3$, (*d*) $\overset{\oplus}{C}H_2.CH_2.CH_2.CH_3$.

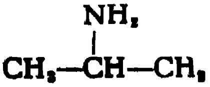
8. Number of stereoisomeric forms of the compound, $CH_3CH=CH.CHBr.CH_3$ is

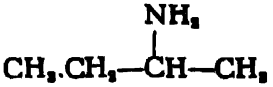
(*a*) Three, (*b*) Six, (*c*) Two, (*d*) Four.

9. Which of the following compounds can occur in enantiomeric forms :

(*a*)

$CH_3-\overset{\overset{\large CH_3}{|}}{C}H-COOH$

(*b*) $CH_3.CH=CH.CH_2CH_3$

(*c*)

$CH_3-\overset{\overset{\large NH_2}{|}}{C}H-CH_3$

(*d*)

$CH_3.CH_2-\overset{\overset{\large NH_2}{|}}{C}H-CH_3$

10. Which of the following statements is false ?

(*a*) A tertiary carbocation is more stable than a primary carbocation.

(*b*) A tertiary radical is more stable than a secondary radical.

(*c*) A primary carbocation is more stable than secondary.

(*d*) A secondary radical is more stable than primary.

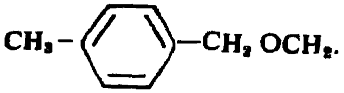
11. The pmr spectrum of $CH_3-CH_2-O-CH_2-CH_3$ shows

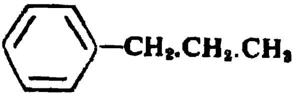
(*a*) two peaks (both triplets)
(*b*) four peaks (all doublets)
(*c*) two peaks (one triplet and the other doublet)
(*d*) two peaks (one triplet and the other quartet).

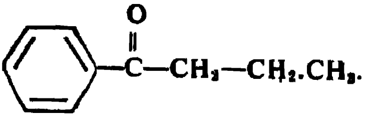
12. The pmr spectrum of a compound shows the following peaks ?

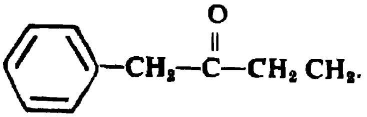
(*i*) A singlet, 5H (δ 7·22) ;
(*ii*) A singlet, 2H, (δ 3·59) ;
(*iii*) A 1 : 3 : 3 : 1 quartet. 2H (δ 2·77) ; and
(*iv*) A 1 : 2 : 1 triplet, 3H (δ 0·977),

Which of the following structures correspond to these peaks ?

(*a*)


(*b*)


(*c*)


(*d*)


KEY

1. (*c*)	2. (*b*)	3. (*b*)	4. (*b*)
5. (*c*)	6. (*c*)	7. (*b*)	8. (*d*)
9. (*d*)	10. (*c*)	11. (*d*)	12. (*d*)

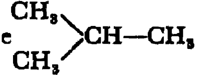
PART II—ORGANIC COMPOUNDS

13

Alkanes or Paraffins

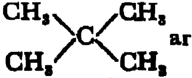
1. **Nomenclature of the Paraffins.**—The class name for saturated aliphatic hydrocarbons is alkanes or paraffins. The paraffins are represented by the general formula C_nH_{2n+2} and are given this name because they are quite non-reactive. The name comes from the Latin words *parum* (=little) and *affinis* (affinity). There are at least three systems in use for naming paraffins and in all the three, the class suffix remains *-ane.*

(*i*) In the **trivial system** of nomenclature, the straight-chain paraffins are termed *normal* usually abbreviated to *n-* ; those with a branched-chain like



$$\begin{matrix}CH_3\diagdown \\ \quad CH{-}CH_3 \\ CH_3\diagup\end{matrix}$$

(containing a tertiary carbon atom—one directly linked to three other carbon atoms) are termed *iso* whereas other containing a quaternary carbon atom (attached to four other carbon atoms), *e.g.*,



$$\begin{matrix}CH_3\diagdown & & \diagup CH_3 \\ & C & \\ CH_3\diagup & & \diagdown CH_3\end{matrix}$$

are called *neo.*

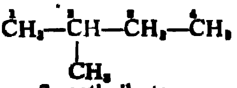
The first four paraffins have special names related to their history ; from the fifth onwards the names follow the Latin or Greek numerals which indicate the number of carbon atoms in the molecule as given below :

Formula	*Name*	*Formula*	*Name*
CH_4	Methane	C_9H_{20}	Nonane
C_2H_6	Ethane	$C_{10}H_{22}$	Decane
C_3H_8	Propane	$C_{12}H_{26}$	Dodecane
C_4H_{10}	Butane	$C_{20}H_{42}$	Eisocane
C_5H_{12}	Pentane	$C_{30}H_{62}$	Triacontane
C_6H_{14}	Hexane	$C_{50}H_{102}$	Pentacontane
C_7H_{16}	Heptane	$C_{70}H_{142}$	Heptacontane
C_8H_{18}	Octane	$C_{80}H_{162}$	Octaneontane

The univalent radicals which are formed by the removal of one hydrogen atom of the paraffins are termed alkyl groups or radicals (*See page 1·113*).

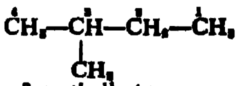
(*ii*) According to another system, branched-chain paraffins are named as substituted methanes. The most highly branched carbon atom is termed the methane nucleus and the alkyl groups attached to this carbon atom are named in alphabetical order. Thus every name indicates the structure of the compound.

(*iii*) In the **IUPAC system**, the longest possible straight chain is selected and the paraffin is named as the derivative of this alkane. *The carbon atoms constituting the straight chain are so numbered that the numbers, used to indicate the positions of side-chains, are the lowest possible.* Various groups present are arranged alphabetically. For example,



$$\overset{1}{C}H_3-\underset{\underset{CH_3}{|}}{\overset{2}{C}H}-\overset{3}{C}H_2-\overset{4}{C}H_3$$

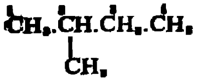
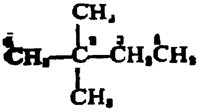
2-methylbutane
(Right)



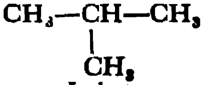
$$\overset{4}{C}H_3-\underset{\underset{CH_3}{|}}{\overset{3}{C}H}-\overset{2}{C}H_2-\overset{1}{C}H_3$$

3-methylbutane
(Wrong)

A few examples of the three systems of nomenclature are given below :

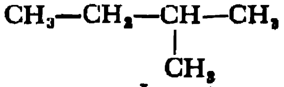
Formula	*I System*	*II System*	*III System*
$CH_3.CH_2.CH_2.CH_3$	*n*-butane	...	butane
 $\overset{1}{C}H_3.\underset{\underset{CH_3}{\lvert}}{\overset{2}{C}H}.\overset{3}{C}H_2.\overset{4}{C}H_3$	Isopentane	dimethylethyl methane	2-methyl-butane
 $\overset{1}{C}H_3-\underset{\underset{CH_3}{\lvert}}{\overset{\overset{CH_3}{\lvert}}{\overset{2}{C}}}-\overset{3}{C}H_2\overset{4}{C}H_3$	Neohexane	trimethyl-ethylmethane	2, 2-dimethyl-butane

Four branched alkanes have trivial names recognized in the 1957 IUPAC Rules. These are :



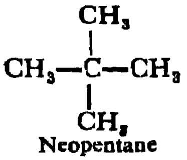
$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_3$$

Isobutane



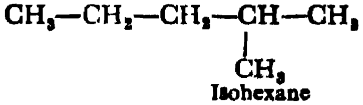
$$CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$$

Isopentane



$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

Neopentane



$$CH_3-CH_2-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$$

Isohexane

These names are, however, to be used only for the unsubstituted alkanes.

2. **Occurrence.**—The most important source of alkanes is petroleum or the natural gas associated with it. Fuel gases obtained from coal, *e.g.*, coal gas, etc., contain these hydrocarbons in small amounts. Methane is formed during the decay of plants or animal tissues.

3. **General Methods of Preparation.**—One of the characteristics of a homologous series is that its various homologues can be prepared by similar methods. This gives rise to the general methods of preparation of a particular homologous series. The general methods of preparation of the paraffins are given below :

(*i*) *By heating a mixture of the anhydrous sodium salt of a fatty acid with soda lime** (NaOH+CaO).

$$\underset{\text{Sod. salt of the fatty acid}}{R|\overline{COONa} + \underset{\text{Soda lime}}{\overline{NaO}}|H} \xrightarrow[\Delta]{CaO} \underset{\text{Paraffin}}{RH} + Na_2CO_3$$

$$\underset{\text{Sod. acetate}}{CH_3|\overline{COONa}} + \overline{NaO}|H \xrightarrow[\Delta]{CaO} \underset{\text{Methane}}{CH_4} + Na_2CO_3$$

For the lower homologues the yield is good but it is poor for the higher ones. The process of elimination of carbon dioxide from a carboxylic acid is known as *decarboxylation.*

(*ii*) *By reducing alkyl halides* (*dissolved in acetic acid*), by dissolving metals, *e.g.*, zinc and acetic acid or hydrochloric acid, zinc and sodium hydroxide, *zinc-copper couple,*† *or aluminium amalgam and ethanol,* etc. It is no longer considered that 'nascent' hydrogen is the reducing agent. It is now believed that reduction is due to electron transfer from the metal to the substrate.

$$\underset{\text{from Zn/Cu couple}}{Zn} \rightarrow Zn^{2+} + \underset{\text{electron}}{2e^-}$$

$$RX + e^- \rightarrow \overset{-}{X} + R\cdot \xrightarrow{e^-} \overset{-}{R}:$$

$$\overset{-}{R}: + C_2H_5OH \rightarrow R{-}H + {}^-OC_2H_5 \qquad (g.\text{-}v.g.)‡$$

Alkyl halide may also be reduced catalytically using palladium as catalyst (*catalytic hydrogenolysis*).

$$RI + H_2 \longrightarrow RH + HI \qquad (v.g.)$$

Iodides are conveniently reduced by heating with concentrated hydriodic acid (571K HI) at 425K under pressure in a sealed tube.

$$RI + HI \longrightarrow RH + I_2 \qquad (g.\text{-}ex.)$$

Primary and secondary alkyl halides may be conveniently reduced with lithium aluminium hydride, $LiAlH_4$. It is quickly oxidised by water vapour in the air, so it is used in a dry organic solvent. Alkyl halide is treated with $LiAlH_4$ and the intermediate complex is hydrolysed with dilute acid.

$$4RX + LiAlH_4 \longrightarrow 4RH + LiAlX_4$$

(*iii*) *By treating alkyl halide* (*preferably the bromide or iodide*) *solution in dry ether with metallic sodium* (**Wurtz Synthesis**—1854).

---

* Soda lime is obtained by saturating lime with caustic soda solution and drying the product. This serves to dilute the strong action of caustic soda. It does not etch glass like caustic soda. CaO stands for soda lime here.

The delta symbol (Δ) indicates the application of heat.

† Zinc-copper couple consists of the pieces of zinc coated with copper obtained by immersing zinc pieces in copper sulphate solution. It is a valuable reducing agent. Similarly, aluminium amalgam is obtained by dipping small pieces of aluminium foil in mercuric chloride solution. The couple or the amalgam obtained is washed thoroughly with water and then with alcohol.

‡ The yield of certain reactions is given by arbitrary symbols in parentheses which have been explained in the preface.

Two molecules of the alkyl halide react with two atoms of sodium and a hydrocarbon containing double the number of carbon atoms present in the alkyl halide is produced.

$$\underset{\substack{\text{Alkyl halide}\\\text{one molecule}}}{R}\boxed{X + 2Na + X}\underset{\substack{\text{Alkyl halide}\\\text{second molecule}}}{R} \longrightarrow \underset{\text{Paraffin}}{R{-}R} + 2NaX$$

$$\underset{\substack{\text{Methyl}\\\text{iodide}}}{CH_3}\boxed{I + 2Na + I}\underset{\substack{\text{Methyl}\\\text{iodide}}}{CH_3} \longrightarrow \underset{\text{Ethane}}{CH_3{-}CH_3} + 2NaI$$

If instead of one alkyl halide, a mixture of two different alkyl halides (say, CH_3I and C_2H_5I) is taken we get a mixture of three hydrocarbons.

$$\underset{\substack{\text{Methyl}\\\text{iodide}}}{CH_3}\boxed{I + 2Na + I}\underset{\substack{\text{Ethyl}\\\text{iodide}}}{C_2H_5} \longrightarrow \underset{\text{Propane}}{CH_3{-}C_2H_5} + 2NaI$$

Two molecules of CH_3I will react to give C_2H_6 (ethane) as given above and two molecules of ethyl iodide will react to give butane.

This reaction has been found to give good yield for paraffins of high molecular weight containing even number of carbon atoms. With tertiary alkyl halides the reaction generally fails. *Methane cannot be prepared by this method.*

Mechanism of the Reaction. Two mechanisms have been suggested for the Wurtz reaction.

(*a*) Intermediate formation of an Organo-metallic compound. Formation of *n*-butane from ethyl iodide can be explained as follows :

$$C_2H_5{-}I + 2Na \longrightarrow \underset{\text{Organo-metallic cpd.}}{\overset{-}{C_2H_5}\overset{+}{Na}} + NaI$$

$$\overset{-}{C_2H_5}\overset{+}{Na} + C_2H_5I \longrightarrow \underset{n\text{-butane}}{C_2H_5{-}C_2H_5} + NaI$$

(*b*) Intermediate formation of Free radicals. For example, the above reaction can also be explained as under :

$$C_2H_5{-}I + Na \longrightarrow \underset{\text{Free radical}}{C_2H_5^{\cdot}} + NaI$$

$$C_2H_5^{\cdot} + C_2H_5^{\cdot} \longrightarrow \underset{n\text{-butane}}{C_2H_5{-}C_2H_5}$$

Free radicals also undergo *disproportionation*, *i.e.*, one radical gains hydrogen at the expense of the other which loses hydrogen.

$$C_2H_5^{\cdot} + C_2H_5^{\cdot} \longrightarrow \underset{\text{Ethane}}{C_2H_6} + \underset{\text{Ethylene}}{C_2H_4}$$

This accounts for the presence of ethylene and ethane in the butane obtained by Wurtz synthesis.

There is sufficient evidence in favour of both the mechanisms. It is even possible that both are involved simultaneously.

(iv) *By the electrolysis of a concentrated aqueous solution of the alkali (sodium or potassium) salt of a fatty acid* (**Kolbe's electrolytic reaction**—1848).

At anode :

$$\underset{\text{Two ions of fatty acid}}{\begin{matrix}\text{RCOO}\\ +\\ \text{RCOO}\end{matrix}} \longrightarrow \underset{\text{Paraffin}}{\begin{matrix}\text{R}\\ |\\ \text{R}\end{matrix}} + 2CO_2 + 2e^- \text{ (electrons lost to anode)}$$

At cathode :

$$2H_2O + 2e^- \longrightarrow 2OH^- + H_2\uparrow \text{ (electrons accepted from cathode)}$$

The yields are *g.-v.g.* if only a single substance is electrolysed. *Methane cannot be prepared by this method.*

Mechanism of the Reaction. The mechanism of the reaction is not clear. Possible mechanism suggested is *via Intermediate formation of Free Radicals.* For example, formation of *n*-butane, ethane, ethylene and ethyl propionate, sodium propionate solution is electrolysed, is explained as follows :

$$C_2H_5COONa \rightleftharpoons C_2H_5COO^- + Na^+$$

$$\underset{\textit{Propionate ion}}{C_2H_5COO^-} \longrightarrow \underset{\textit{Free propionate radical}}{C_2H_5COO^\cdot} + \textit{One electron given to anode}$$

Free propionate radical further breaks up into the ethyl radical and carbon dioxide (*Fragmentation*).

$$C_2H_5COO^\cdot \longrightarrow C_2H_5^\cdot + CO_2$$

Free ethyl radicals then give

(*i*) *n*-butane, by combination $2C_2H_5^\cdot \longrightarrow C_2H_5—C_2H_5$.

(*ii*) ethane and ethylene by disproportionation

$C_2H_5^\cdot + C_2H_5^\cdot \longrightarrow C_2H_6 + C_2H_4$ and

(*iii*) ethyl propionate by combination with free propionate radical.

$$C_2H_5COO^\cdot + C_2H_5^\cdot \longrightarrow C_2H_5COOC_2H_5$$

(v) *By heating an alcohol ROH, or a carbonyl compound (aldehyde or ketone) with excess of concentrated hydriodic acid at high temperature, under pressure in a sealed tube. The reduction is usually carried out in the presence of a small amount of red phosphorus which regenerates the hydriodic acid from the iodine formed.*

$$\underset{\text{Alcohol}}{ROH} + 2HI \xrightarrow{\text{Red P, 420K}} \underset{\text{Paraffin}}{RH} + H_2O + I_2 \qquad (\textit{g.-ex.})$$

$$CH_3.CO.CH_3 + 4HI \xrightarrow{\text{Red P, 420K}} CH_3.CH_2.CH_3 + 2I_2 + H_2O \; (\textit{v.g.})$$

$$RCOOH + 6HI \xrightarrow{\text{Red P, 470K}} RCH_3 + 2H_2O + 3I_2$$

Carbonyl compounds (preferably ketones) may also be reduced with amalgamated zinc and concentrated hydrochloric acid (*Clemmensen reduction*) and fatty acids by heating with hydrogen under pressure in presence of nickel catalyst.

$$\mathrm{RCOR} \xrightarrow{e^-\,;\,H^+} \mathrm{RCH_2R}$$

$$\mathrm{R'COOH} + 3H_2 \xrightarrow{Ni} \mathrm{R'CH_3} + 2H_2O$$

The yield is very good for higher alkanes.

(*vi*) *By hydrogenation of unsaturated hydrocarbons in presence of finely-divided nickel at 570K*—(**Sabatier and Senderens Reaction**).

$$\underset{\text{Olefin}}{C_nH_{2n}} + H_2 \xrightarrow{\text{Ni 570K}} \underset{\text{Paraffin}}{C_nH_{2n+2}} \qquad (ex.)$$

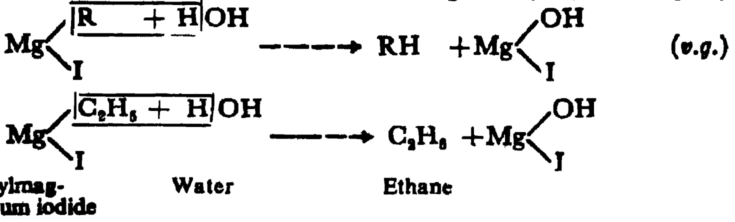
$$\underset{\text{Ethylene}}{CH_2{=}CH_2} + H_2 \xrightarrow{\text{Ni, 570K}} \underset{\text{Ethane}}{CH_3{-}CH_3}$$

$$\underset{\text{Acetylene}}{CH{\equiv}CH} + 2H_2 \xrightarrow{\text{Ni, 570K}} \underset{\text{Ethane}}{CH_3{-}CH_3}$$

No unsaturated hydrocarbon contains only one carbon atom, hence this method cannot be used to prepare methane.

(*vii*) *By the action of water on Grignard reagent* (*Alkylmagnesium halides*). *An alkyl halide* (*preferably an iodide*) *is heated with dry magnesium powder in dry ether and the Grignard reagent so obtained is then decomposed by water.*

$$\mathrm{RI} + \mathrm{Mg} \xrightarrow{\text{Dry ether}} \mathrm{R{-}Mg{-}I} \quad (\textit{Grignard reagent})$$



$$\mathrm{Mg}\begin{cases}\boxed{R\quad + H}OH \\ I\end{cases} \longrightarrow RH + \mathrm{Mg}\begin{cases}OH \\ I\end{cases} \qquad (e.g.)$$

$$\underset{\text{Ethylmagnesium iodide}}{\mathrm{Mg}\begin{cases}\boxed{C_2H_5 + H}OH \\ I\end{cases}} \underset{\text{Water}}{} \longrightarrow \underset{\text{Ethane}}{C_2H_6} + \mathrm{Mg}\begin{cases}OH \\ I\end{cases}$$

(*viii*) Long-chain alkanes can be prepared by coupling of alkylboranes (*see page 2·28*) in presence of $AgNO_3$ containing NaOH at 300K. For example

$$\underset{\text{1-Pentene}}{6CH_3(CH_2)_2CH{=}CH_2} \xrightarrow{2B_2H_6} \underset{\text{Pentylborane}}{[2CH_3(CH_2)_3CH_2^-]_3B}$$

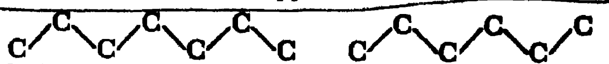
$$\xrightarrow[NaOH]{AgNO_3} \underset{\text{Decane}}{3CH_3(CH_2)_2CH_2{-}CH_2(CH_2)_3CH_3}$$

4. General Physical Properties of the Paraffins.—The paraffins from C_1 to C_4 are colourless, odourless gases while C_5 to C_{17} are colourless, odourless liquids and higher ones are solids. They are insoluble in polar solvents like water, but soluble in non-polar solvents, *e.g.*, various organic solvents like alcohol, ether and benzene. Their solubility decreases with increase in their molecular weights. Other physical constants (*e.g.*, melting points, boiling points, density, etc.) show a regular gradation. This, however, holds good only for the normal paraffins. The processes of boiling and melting require overcoming the intermolecular forces of a liquid and solid ; the boiling points and melting points rise because these intermolecular forces increase as the molecule gets larger. The boiling point increases by 20-30K for each carbon added to the chain. The increase in melting point is not so regular. This is because intermolecular forces in a crystal depend not only upon the size of the molecules but also upon how well they fit into the crystal lattice. They are all less dense than water (highest density about 0·8).

In the case of isomeric paraffins, the normal one always has the highest b.p. and m.p. Generally, greater the branching in a paraffin, the lower is the boiling point.

Name	M.P.	B.P.	Name	M.P.	B.P.
Methane	89K	111·6K	Isobutane	114K	261 K
Ethane	101K	184·7K	*n*-Pentane	143·8K	309 K
Propane	83·1K	228·5K	Isopentane	113K	301·1K
n-Butane	134·7K	272·45K	Neopentane	253K	282·5K

Alkanes with even number of carbon atoms have higher m.p. than the next lower and next higher alkanes having odd number of carbon atoms. This is probably due to the fact that alkanes with an odd number of carbon atoms have their end-carbon atoms on the same side of the molecule and the even-numbered carbon atom alkanes have their end-carbon atoms on opposite sides of the molecules.



Odd-numbered C-chain Even-numbered C-chain

Alkanes with even number of carbon atoms pack so as to permit greater intermolecular attraction and therefore have slightly higher melting point.

The position of IR absorption region of CH group (stretch) in alkanes depends on the nature of carbon atom (whether primary, secondary or tertiary). Various regions are:

C—H *Stretching absorption frequencies* :

$-CH_3$ 2975—2950 and 2885—2860 cm^{-1} (*m*)
$>CH_2$ 2944—2915 and 2870—2845 cm^{-1} (*m*)
$-\!\!\!\!>CH$ 2900 – 2880 cm^{-1} (*w*)

C—H *Deformation absorption frequencies* :

$-CH_3$ 1470—1435 (*m*) and 1385—1370 cm^{-1} (*m*)
$>CH_2$ 1480—1440 cm^{-1} (*m*)

Skeletal vibrations :

iso, Me_2CH— 1175—1165 cm^{-1} (*s*)
neo, Me_3C— 1255—1245 cm^{-1} (*s*)

5. General Chemical Properties of the Paraffins.— Under ordinary conditions, the paraffins are quite inert towards common reagents such as acids, alkalis and oxidising agents. It has, however, been shown in recent years that the paraffins are reactive if the right conditions are used. The general reactions shown by them are :

(1) **Halogenation.** Chlorination is brought about by light, heat, or catalysts (called *halogen carriers*, *e.g.*, iron filings) and the extent to which chlorination occurs depends largely on the amount of chlorine used. For example, during chlorination of methane in diffused sunlight the four hydrogen atoms are successively replaced by chlorine atoms.

$$CH_4 + Cl_2 \rightarrow HCl + CH_3Cl \quad (\textit{methyl chloride})$$
$$CH_3Cl + Cl_2 \rightarrow HCl + CH_2Cl_2 \quad (\textit{methylene chloride})$$
$$CH_2Cl_2 + Cl_2 \rightarrow HCl + CHCl_3 \quad (\textit{chloroform})$$
$$CHCl_3 + Cl_2 \rightarrow HCl + CCl_4 \quad (\textit{carbon tetrachloride})$$

This type of replacement reaction is known as *substitution*. *In a substitution reaction, an atom or a group present in a compound is replaced by another without the compound undergoing any change in its structure.* The products thus obtained are called *substitution products*.

In higher members mixtures of all possible isomeric monochlorides are obtained. According to *Markownikoff* (1875) the *order of substitution is tertiary hydrogen** > *secondary* > *primary*.

Bromination is similar but not so vigorous as chlorination. With iodine the reaction is reversible.

$$CH_4 + I_2 \rightleftharpoons CH_3I + HI$$

Iodination is, therefore, carried out in the presence of an oxidising agent such as iodic acid, nitric acid, mercuric oxide, etc., which destroys the hydriodic acid as it is formed

$$5HI + HIO_3 \rightarrow 3I_2 + 3H_2O$$

Direct fluorination is usually explosive (*cf.* chlorination of methane in bright sunlight which is also explosive).

$$CH_4 + 2F_2 \rightarrow C + 4HF$$
$$CH_4 + 2Cl_2 \rightarrow C + 4HCl$$

of Halogenation (*See Part 1, Chapter 10, page* 1·162)

Halogenation of paraffins is an oxidative process. Oxidation involves complete or relative loss of electrons by an atom. Before halogenation, the electron pair constituting the C—H bond is nearly equally shared between the two atoms. After halogenation, the

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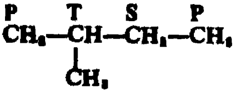
* Hydrogen atoms attached to primary, secondary and tertiary carbon atoms are known as primary, secondary and tertiary hydrogen atoms, respectively. A carbon atom is termed primary, secondary or tertiary according as it is attached to one, two or three other carbon atoms. For example, in the *isopentane* given below :



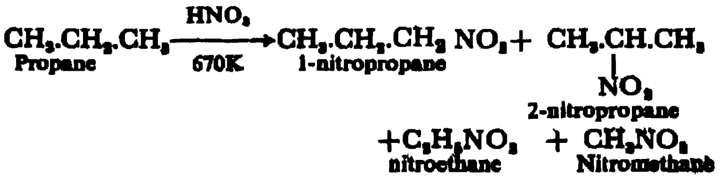
$$\overset{P}{CH_3}—\underset{\displaystyle CH_3}{\overset{T}{CH}}—\overset{S}{CH_2}—\overset{P}{CH_3}$$

Isopentane

there are three primary carbon atoms, one secondary carbon atom and one tertiary carbon atom. In this compound there are nine primary hydrogen atoms attached to three primary carbon atoms. Similarly there are two secondary hydrogen atoms attached to one secondary carbon atom and one tertiary hydrogen atom attached to the tertiary carbon atom.

electron pair of the C—X bond is nearer the halogen atom. The carbon atom has thus lost some share in the electron pair and is said to be oxidised.

(2) **Nitration.** Paraffins react with nitric acid under certain conditions when a hydrogen atom is replaced by *nitro group*, NO_2. The process is termed *nitration*. Nitration is carried out in vapour phase between 420-720K when a mixture of all possible mono-nitro derivatives (obtained direct or after *chain fission*) is obtained. For example, by nitration of propane, we get



$$\underset{\text{Propane}}{CH_3.CH_2.CH_3} \xrightarrow[670K]{HNO_3} \underset{\text{1-nitropropane}}{CH_3.CH_2.CH_2\,NO_2} + \underset{\text{2-nitropropane}}{\underset{\underset{\displaystyle NO_2}{|}}{CH_3.CH.CH_3}}$$

$$+\underset{\text{nitroethane}}{C_2H_5NO_2} + \underset{\text{Nitromethane}}{CH_3NO_2}$$

The ease with which various hydrogen atoms are replaced is in accordance with the Markownikoff's rule for halogenation.

(3) **Sulphonation.** When a normal paraffin from hexane onwards is treated with oleum, a hydrogen atom is replaced by a sulphonic group, $—SO_3H$. The process of replacement is known as *sulphonation*. The ease of replacement of hydrogen atoms is : tertiary > secondary > primary (*cf.* halogenation and nitration). For example, sulphonation of isobutane yields 2-methyl-2-propane-sulphonic acid.

$$\underset{\text{Isobutane}}{(CH_3)_3C}\boxed{H \quad + \quad HO}.SO_3H \underset{\substack{\text{Oleum or}\\ \text{fuming sulphuric}\\ \text{acid } (H_2SO_4+SO_3)}}{} \rightarrow \underset{\substack{\text{2-Methyl-2-propane-}\\ \text{sulphonic acid}}}{(CH_3)_3C.SO_3H} + H_2O$$

(4) **Oxidation.** (*a*) COMBUSTION. Paraffins readily burn with a non-luminous flame in excess of air or oxygen to give carbon dioxide and water. These form explosive mixture with air or oxygen.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

$$2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$$

(*b*) OXIDISING AGENTS, *e.g.*, alkaline potassium permanganate, readily oxidise a *tertiary* hydrogen to a hydroxyl group. For instance, isobutane gives *tert*-butyl alcohol when oxidised.

$$\underset{\text{isobutane}}{(CH_3)_3CH} + [O] \xrightarrow{KMnO_4} \underset{\text{tert-butyl alcohol}}{(CH_3)_3COH}$$

A tertiary carbon atom is oxidised with relative ease because the alkyl groups are weakly electronegative as compared with hydrogen and possess a relatively low attraction for electrons. Thus the electron density about a tertiary carbon atom is relatively high and accounts for its oxidation with relative ease.

(*c*) CATALYTIC OXIDATION of methane gives methanol, CH_3OH and formaldehyde, HCHO whereas that of higher homologues (C_{18}—) produces long-chain fatty acids.

(*i*) When a mixture of methane and oxygen in the ratio 9 : 1 is compressed to 100 atmospheres and passed through copper tubes at 470K, methane is oxidised to methanol.

$$2CH_4+O_2 \rightarrow \underset{\text{Methanol}}{2CH_3OH}$$

(*ii*) *When methane mixed with oxygen is passed over a heated catalyst, e.g., molybdenum oxide, it is oxidised to methanal.*

$$CH_4 + O_2 \longrightarrow \underset{\text{Formaldehyde}}{HCHO} + H_2O$$

$$(iii)\quad \underset{\substack{\text{Higher}\\ \text{alkane}}}{2RCH_3} + \underset{\substack{\text{From}\\ \text{air}}}{3O_2} \xrightarrow[\substack{\text{acetate}\\ \text{370-430K}}]{\text{Manganese}} \underset{\substack{\text{Higher}\\ \text{fatty acid}}}{2RCOOH} + 2H_2O$$

(*d*) SLOW COMBUSTION. Recently it has been found that when methane or ethane is treated with oxygen at high pressure and comparatively low temperature, the hydrogen atoms change to (OH) groups successively, the end products are CO_2+H_2O.

$$\begin{tikzcd}
\underset{\text{Methane}}{CH_4} \arrow[r, "O"] & \underset{\text{Methanol}}{CH_3OH} \arrow[r, "O"] & CH_2(OH)_2 \arrow[r, "-H_2O"] & \underset{\text{Formaldehyde}}{HCHO} \arrow[d, "O"] \\
 & & CO_2+H_2O & \underset{\text{Formic acid}}{HCOOH} \arrow[l, "O"']
\end{tikzcd}$$

(5) **Thermal Decomposition, Pyrolysis or Cracking** When vapours of higher paraffins are passed through a hot metal tube (775-975K), it breaks up to yield smaller molecules. For example, on cracking propane, the possible products are :

$$\underset{\text{Propylene}}{C_3H_6} + H_2 \longleftarrow \underset{\text{Propane}}{C_3H_8} \longrightarrow \underset{\text{Methane}}{CH_4} + \underset{\text{Ethylene}}{C_2H_4} \rightarrow 2CH_4+C$$

Large quantities of high-boiling fractions of petroleum are converted into low-boiling gasoline by cracking.

Propylene and hydrogen are produced from propane as a result of fission of C—H linkages whereas methane and ethylene are obtained due to the fission of C—C linkages.

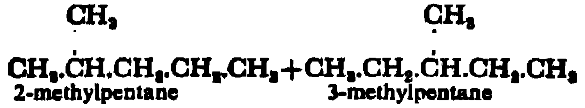
In the case of higher alkanes fission of C—C linkages occurs more readily. The presence of catalysts (like oxides of chromium, vanadium and molybdenum), however, accelerates the fission of C—H linkages. Pyrolysis in the presence of catalysts is used in the manufacture of alkenes.

Mechanism of cracking is still obscure. Out of the many mechanisms suggested the one *via the formation of free radicals is* highly favoured. For example, in the cracking of propane,

$$\begin{tikzcd}
\underset{\text{Propane}}{CH_3CH_2CH_3} \arrow[r] \arrow[d] & CH_3CH_2—\dot{C}H_2+H^{\cdot} \arrow[r] & CH_3CH{=}CH_2+H_2 \\
\underset{(\textit{Free radicals})}{CH_3—CH_2^{\cdot}+CH_3^{\cdot}} \arrow[rr, "\text{Disproportionation}"] & & \underset{\text{Ethylene}}{CH_2{=}CH_2} + \underset{\text{Methane}}{CH_4}
\end{tikzcd}$$

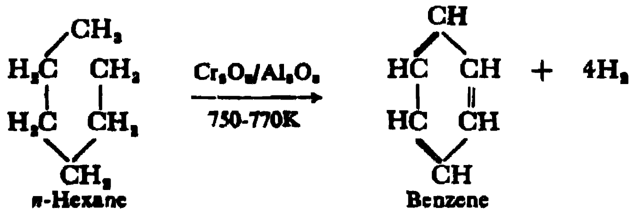
(6) **Isomerisation.** *n*-Alkanes when heated with aluminium chloride at 570K isomerise to give branched-chain alkanes. For example,

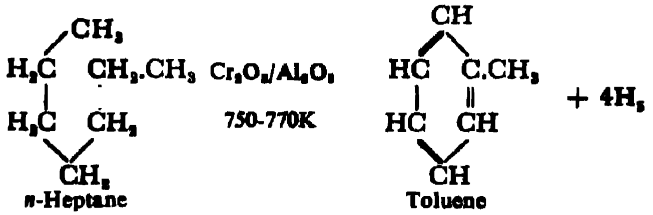
$$\underset{n\text{-hexane}}{CH_3CH_2.CH_2.CH_2.CH_2.CH_3} \xrightarrow[\text{Isomerisation}]{AlCl_3/570K}$$



$$\underset{\text{2-methylpentane}}{CH_3.\overset{CH_3}{\overset{|}{C}}H.CH_2.CH_2.CH_3} + \underset{\text{3-methylpentane}}{CH_3.CH_2.\overset{CH_3}{\overset{|}{C}}H.CH_2.CH_3}$$

(7) **Aromatisation.** Paraffins containing six or more carbon atoms when heated under pressure in presence of suitable catalysts get cyclised to give aromatic compounds. For example, *n*-hexane when passed under pressure over a heated catalyst (chromic oxide carried on an alumina support) at 750-770K gives benzene and hydrogen is set free.





6. **Thermodynamics and Kinetics of the Reactions of Methane with Halogens.**—As stated on pages 2·12 and 2·13 order of reactivity of halogens in the substitution reaction is

fluorination > chlorination > bromination > iodination

The relative reactivity of one substance towards another is measured by the rate at which these two substances react. Fluorine its most reactive and if special precautions are not taken, fluorination of methane is explosive. Chlorination can be easily controlled, bromination is slow and iodine is very unreactive.

Mechanism of chlorination of methane has been discussed on page 1·162. Assuming that the mechanisms for fluorination, bromination and iodination are the same as for the chlorination of methane, we can account for the order of reactivity of the halogens on the basis of thermodynamic quantities ΔH and E_{act} for the various steps involved in halogenation in each case.

Fluorination	ΔH (kJ mol^{-1})	E_{act} (kJ mol^{-1})
(*i*) $F_2 \rightarrow 2F^{\cdot}$	+159·1	+159·1
(*ii*) $F^{\cdot} + CH_4 \rightarrow HF + CH_3^{\cdot}$	−133·9	+5·1
(*iii*) $CH_3^{\cdot} + F_2 \rightarrow CH_3F + F^{\cdot}$	−292·9	small

Overall $\Delta H = -426·8$

The chain-initiating step (*i*) in fluorination is highly endothermic and has, therefore, a high energy of activation (= +159·1 kJ mol^{-1}). If rate of reaction were dependent only on this step, fluorine would be very unreactive. One chain-initiating step is followed by thousands of chain-propagation steps [(*ii*) and (*iii*)] which in fluorination have very small energies of activation. As a result, the high activation energy of step (*i*) is not an impediment to the fluorination reaction.

If a chain reaction has to proceed, the chain-propagating steps must necessarily have low energies of activation If it is not so, the highly reactive intermediates (free radicals) will be consumed by the chain-terminating steps before the chain progresses very far.

Overall heat of reaction, ΔH for fluorination is very large. As the reaction proceeds, heat of reaction accumulates in the reaction medium raising its temperature thereby. At higher temperatures there will be more chain-initiating steps and thus additional chains.

These two factors, *viz.* (*i*) the low energy of activation for the chain-propagating steps and (*ii*) the large overall heat of reaction (ΔH), account for the high reactivity and explosive violence with which fluorine reacts with methane.

Chlorination	ΔH (kJ mol^{-1})	E_{act} (kJ mol^{-1})
(*i*) $Cl_2 \rightarrow 2Cl^{\cdot}$	+242·7	+242·7
(*ii*) $Cl^{\cdot} + CH_4 \rightarrow HCl + CH_3^{\cdot}$	+4·2	+15·9
(*iii*) $CH_3^{\cdot} + Cl_2 \rightarrow CH_3Cl + Cl^{\cdot}$	−106·7	small

Overall $\Delta H = -102·5$

On the basis of thermodynamic quantities ΔH and E_{act}, we can explain why fluorination is more rapid as compared to chlorination as follows :

(*i*) Higher energy of activation of the first chain-propagating step in chlorination ($E_{act} = +15·9$ kJ mol^{-1}) as compared to that of the corresponding step in fluorination ($E_{act} = +5·1$ kJ mol^{-1}).

(*ii*) Greater energy required for the chain-initiating step in chlorination ($E_{act} = +242·7$ kJ mol^{-1} as compared to much lower $E_{act} = +159·1$ kJ mol^{-1} for fluorination) also has some effect.

(*iii*) Most important role is played by the much greater overall heat of reaction in fluorination ($\Delta H = -426·8$ kJ mol^{-1} as compared to −102·5 kJ mol^{-1} for chlorination).

Bromination	ΔH (kJ mol^{-1})	E_{act} (kJ/mol^{-1})
(*i*) $Br_2 \rightarrow 2Br^{\cdot}$	$+192{\cdot}5$	$+192{\cdot}5$
(*ii*) $Br^{\cdot} + CH_4 \rightarrow HBr + CH_3^{\cdot}$	$+69$	$+77{\cdot}8$
(*iii*) $CH_3^{\cdot} + Br_2 \rightarrow CH_3Br + Br^{\cdot}$	$-100{\cdot}4$	small

Overall $\Delta H = -31{\cdot}4$

First chain-propagating step in bromination has a very high energy of activation ($E_{act} = +77{\cdot}8$ kJ mol^{-1} in contrast to $+15{\cdot}9$ kJ mol^{-1} for chlorination). In comparison to chlorine, bromine is, therefore, much less reactive towards methane.

Iodination	ΔH (kJ mol^{-1})	E_{act} (kJmol^{-1})
(*i*) $I_2 \rightarrow 2I^{\cdot}$	$+150{\cdot}7$	$+150{\cdot}7$
(*ii*) $I^{\cdot} + CH_4 \rightarrow HI + CH_3^{\cdot}$	$+129{\cdot}7$	$+140{\cdot}2$
(*iii*) $CH_3^{\cdot} + I_2 \rightarrow CH_3I + I^{\cdot}$	$-83{\cdot}7$	small

Overall $\Delta H = +46{\cdot}0$

First chain-propagating step in iodination has much higher energy of activation even when compared to bromination ($+140{\cdot}2$ kJ mol^{-1} *versus* $+77{\cdot}8$ kJ mol^{-1} in bromination). Iodination is, therefore, not a feasible reaction experimentally.

From the above discussion it is clear that the chain-initiating step in not responsible for the observed order of reactivities : $F_2 > Cl_2 > Br_2 > I_2$. Fluorine is much more reactive than iodine even though iodine-iodine bond is weaker than fluorine-fluorine bond and on the basis of this bond strength alone, iodine would be the most reactive of the halogens. This is not so in practice.

We further notice that energy of activation of the first chain-propagating step determines the order of reactivities of the halogens. As E_{act} for this step increases from F to I, the fraction of collisions with energies greater than the energy of activation, decreases and consequently the reactivity decreases.

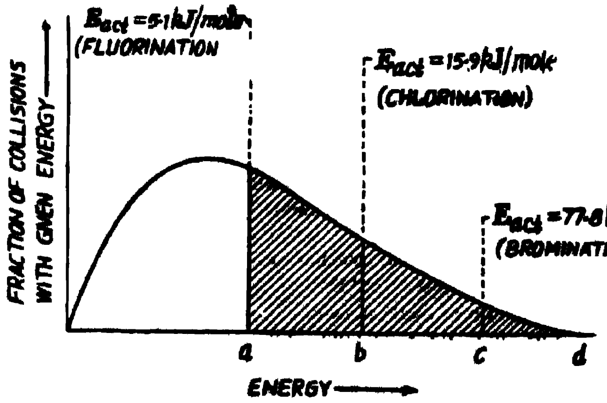
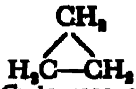
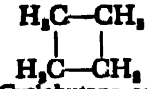
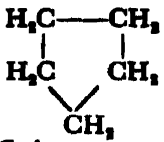


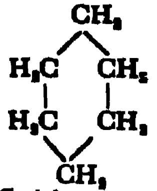
Fig. 13·1—The fraction of collisions with energies greater than the energy of activation at three different E_{act} values is indicated by the area of the shaded strip extending from point *a* to *d*, *b* to *d* and *c* to *d* respectively.

7. Cycloalkanes, Cycloparaffins or Polymethylenes.—These are closed chain hydrocarbons with general formula C_nH_{2n}. Thus they are isomeric with olefins but saturated and quite stable. These are named after corresponding alkanes with the same number of carbon atoms or according to the number of the methylene groups in the molecule. For example,


Cyclopropane or Trimethylene


Cyclobutane or Tetramethylene


Cyclopentane or Pentamethylene


Cyclohexane or Hexamethylene

A brief mention of cycloalkanes is made at this point. A complete discussion of these hydrocarbons will be found in a subsequent chapter.

Cycloparaffins resemble paraffins in their physical properties but have higher boiling points and greater densities than the corresponding alkanes.

Cyclopentane and higher members are quite stable and resemble alkanes. Cyclopropane and cyclobutane rings are comparatively less stable and break when these compounds are treated with bromine in sunlight or with hydriodic acid.

QUESTIONS

Essay Type :

1. Describe general methods of preparation of alkanes and discuss their properties.

2. How do the physical properties of the members of the methane series of hydrocarbons vary with increase of the number of carbon atoms ? What are their chemical characteristics ?

3. Write notes on :

(*a*) Sabatier and Senderens reaction. (*b*) Wurtz Synthesis.
(*c*) Kolbe's Electrolytic method. (*d*) Isomerism of alkanes.

4. How will you prepare the following :

(*a*) *n*-Butane from ethyl bromide. (*b*) *n*-Hexane from *n*-butyric acid.
(*c*) Isopentane from isoamyl iodide. (*d*) Ethane from acetylene.
(*e*) Ethane from propane and *vice versa* ?

5. Explain the mechanism of halogenation of alkanes. What possible evidence you can give in support of the suggested mechanism ?

(*Punjab B.Sc. 1976, 74*)

6. Discuss the free radical mechanism in case of halogenation of alkanes. What have you to say in support of this mechanism ?

In the halogenation of methane with chlorine and bromine atoms, the heats of the reactions under the same conditions are given as below :

$$Cl^{\bullet}+CH_4 \longrightarrow HCl+CH_3^{\bullet}\ ;\ \Delta H=+4{\cdot}2\ kJ,\ E_{act}=15{\cdot}9\ kJ.$$

$$Br^{\bullet}+CH_4 \longrightarrow HBr+CH_3^{\bullet}\ ;\ \Delta H'=+69\ kJ,\ E_{act}\ \text{is not given.}$$

What can you predict about the relative rates of the above reactions with the information provided above ? Give reasons for your answers.

(*Punjab B.Sc. 1974*)

7. Write a short note on: Relative rate of halogenation of ______ in terms of bond dissociation energy. *(Punjab B.Sc. 1975)*

8. Chlorination of *n*-butane in the presence of light gives a mixture ining 68 per cent of 2-chlorobutane and 32 per cent of 1-chlorobutane. Explain why? Write the probable transition state in each case.
(Guru Nanak Dev B.Sc. 1976)

9. Explain the following statements :

(*i*) Chlorination of alkanes is an exothermic reaction and yet it requires high temperature or exposure to high energy UV radiations for its success.

(*ii*) A more stable alkyl radical is formed more easily.

(*iii*) Halogenation in the presence of tetramethyllead proceeds at low temperature than when it is done in its absence.

(*iv*) Iodination of methane does not take place, even when bromination and chlorination take place, in spite of the fact that iodine-iodine bond in the iodine molecule is the weakest. *(Guru Nanak Dev B.Sc. 1976)*

10. Explain why—

(*i*) Halogenation of the paraffins is an oxidative process.

(*ii*) A tertiary carbon atom can be oxidised with relative ease.

Short Answer Type :

1. Write structural formulae for the following :

(*i*) 2, 2-Dimethylbutane.
(*ii*) 4-Ethyl-2, 4-dimethylheptane.
(*iii*) Neohexane.
(*iv*) 3, 4, 4-Trimethylheptane.
(*v*) 5-ethyl-2, 3-dimethyloctane.

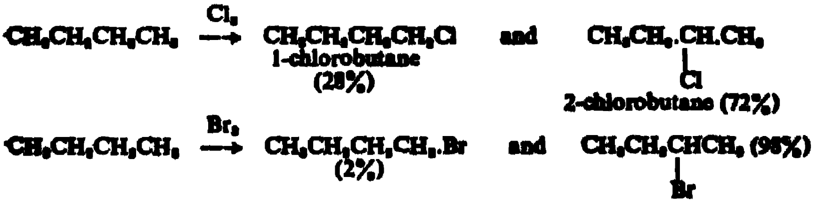
2. Name the following alkanes :

(*i*) $(C_2H_5)_2CH.CH_3$; (*ii*) $(CH_3.CH_2.CH_2)_4C$; (*iii*) $(CH_3)_4C$

3. Which of the following reagents will react with *n*-butane ?

(*i*) Alkaline $KMnO_4$ solution.
(*ii*) Aqueous KOH solution.
(*iii*) Cold dilute nitric acid.
(*iv*) Metallic sodium.
(*v*) Iodine in presence of light.
(*vi*) Bromine in the dark.
(*vii*) Bromine in the presence of light.
(*viii*) Chlorine in the dark.
(*ix*) Chlorine in the presence of light.

4. Although both chlorination and bromination yield mixtures of iso- the relative amounts of various isomers differ markedly depending upon the halogen used. Chlorination gives mixtures in which no isomers greatly predominate whereas in bromination, by contrast, one isomer may predominate to such an extent as to be almost the only product, making up 97-99% of the total mixture, *e.g.*,



$$CH_3CH_2CH_2CH_3 \xrightarrow{Cl_2} \underset{\substack{\text{1-chlorobutane}\\(28\%)}}{CH_3CH_2CH_2CH_2Cl} \quad \text{and} \quad \underset{\text{2-chlorobutane (72\%)}}{CH_3CH_2.\underset{\underset{Cl}{|}}{CH}.CH_3}$$

$$CH_3CH_2CH_2CH_3 \xrightarrow{Br_2} \underset{(2\%)}{CH_3CH_2CH_2CH_2.Br} \quad \text{and} \quad CH_3CH_2\underset{\underset{Br}{|}}{C}HCH_3\ (98\%)$$

In bromination, clearly there is a high degree of *selectivity* as to which hydrogen atoms are to be replaced. This is due to relatively low reactivity of atoms and is an example of a general relationship between *reactivity* and

On the basis of the above how do you account for the fact that not only bromination but also chlorination is a feasible laboratory route to a neopentyl halide, $(CH_3)_3C.CH_2X$?

5. Why would the chlorination of ethane to ethyl chloride be a more practical synthesis than the chlorination of pentane to 1-chloropentane ?

6. An alkane with mol. wt.=72 formed only one monochloro substitution product. Suggest a structure for the alkane.

7. Write equations for the reactions, if any, between :

(*i*) RCOONa+soda-lime. (*ii*) Sodium propionate+soda-lime.
(*iii*) Ethyl iodide+Zn/Cu couple and alcohol. (*iv*) Methyl iodide+HI.
(*v*) Electrolysis of an aqueous solution of sodium acetate.
(*vi*) Ethanol, acetone or a fatty acid+conc. hydriodic acid in presence of red phosphorus.
(*vii*) Ethylene+H_2 in presence of finely divided nickel at 575K.
(*viii*) Acetylene+H_2(Ni, 575K). (*ix*) Ethylmagnesium iodide+water.
(*x*) Methane+chlorine. (*xi*) Propane+nitric acid (670K).
(*xii*) Isobutane+oleum. (*xiii*) Methane+O_2 (burning).
(*xiv*) *Aluminium carbide+water.* (*xv*) *Methane+steam (1000K).*
(*xvi*) *n*-Hexane+$AlCl_3$ at 575K.
(*xvii*) *n*-Hexane or *n*-Heptane+Cr_2O_3/Al_2O_3 at 750-770K.
(*xviii*) 1, 4-Dibromobutane+sodium.

8. Write equations to show :

(*i*) Wurtz reaction.
(*ii*) Kolbe synthesis of alkanes.

(*Delhi B.Sc. 1976 ; B.Sc. Hons. Sub. 1976*)

9. What products are obtained when propane undergoes mono-substitution ? (*Delhi B.Sc. Hons. Sub. 1977*)

10. Discuss reactivities of alkanes towards halogenation.
(*Guru Nanak Dev B.Sc. 1977*)

11. You are given bond dissociation energies (kJ/mole) of the following bonds:

Cl—Cl=242·7 CH_3—H=435·1
H—Cl=430·9 CH_3—CH_3=368·2
CH_3Cl=349·3

Calculate the heat of reaction, ΔH, for the chain-initiating, chain-propagating, and chain-terminating steps in chlorination of methane.

12. Chlorination reactions of certain higher alkanes can be used for laboratory preparation, *e.g.*, for the preparation of neopentyl chloride from neopentane and cyclopentyl chloride from cyclopentane. What structural features of these compounds make this possible ?

13. With the help of the following equations :

(*i*) $CH_3{-}H \rightarrow CH_3. + H^{\cdot}$; $E_{act} = +435$ k
(*ii*) $CH_3CH_2{-}H \rightarrow CH_3CH_2^{\cdot} + H^{\cdot}$; $E_{act} = +410$ kJ
(*iii*) $CH_3CH_3 \rightarrow 2CH_3^{\cdot}$; $E_{act} = +368$ kJ
(*iv*) $CH_3CH_2{-}CH_2CH_3 \rightarrow 2CH_3CH_2^{\cdot}$; $E_{act} = +343$ kJ
(*v*) $CH_3CH_2CH_2{-}CH_3 \rightarrow CH_3CH_2CH_2^{\cdot} + CH_3^{\cdot}$; $E_{act} = +355{\cdot}6$ kJ

account for the following :

(*a*) Thermal cracking of a C—H bond of methane occurs at ~1500K while that of C—H bond of ethane breaks at 800-900K.

(b) During homolysis of ethane at high temperature, the C—C bond breaks more readily than the C—H bonds.

(c) During cracking of n-butane, reaction (iv) occurs more readily than reaction (v) given above.

14. Can isobutane be prepared by Wurtz reaction ?

15. Which higher homologue of methane is likely to be formed during its halogenation ?

16. Of the three isomeric pentanes, which one is expected to yield the largest number of isomeric monochloro derivatives ?

17. How would you obtain n-butane from (i) sec-butyl bromide, (ii) ethyl chloride and (iii) 1-Butene ?

18. Write various possible structural formulae of alkanes with molecular formula C_6H_{14} and write the IUPAC names.

ANSWERS

3. (vii) and (ix), 6. $(CH_3)_4C$ (*neopentane*)

11. (i) $Cl_2 \rightarrow 2Cl^\cdot$; $\Delta H = +242{\cdot}7$ kJ/mole

(ii) $CH_4 + Cl^\cdot \rightarrow HCl + CH_3^\cdot$; $\Delta H = +4{\cdot}2$ kJ/mole

(iii) $CH_3^\cdot + Cl_2 \rightarrow CH_3Cl + Cl^\cdot$; $\Delta H = -106{\cdot}6$ kJ/mole

(iv) $CH_3^\cdot + Cl^\cdot \rightarrow CH_3Cl$; $\Delta H = -349{\cdot}3$ kJ/mole

(v) $CH_3^\cdot + {}^\cdot CH_3 \rightarrow CH_3-CH_3$; $\Delta H = -368{\cdot}2$ kJ/mole

(vi) $Cl^\cdot + Cl^\cdot \rightarrow Cl-Cl$; $\Delta H = -242{\cdot}7$ kJ/mole

12. All hydrogen atoms in each are equivalent, replacement of any one of these by Cl yields the same product.

13. (a) From (i) and (ii), since E_{act} for ethane, C—H cracking reaction is lower, C—H bond in ethane breaks at lower tempetrature.

(b) Since ΔH for reaction (iii) is lower than that in (ii), the C—C bond in ethane breaks more readily than C—H bond.

(c) ΔH for reaction (iv) being lower, it occurs more readily than reaction (v).

14

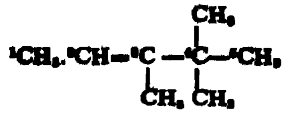
Alkenes or Olefins

1. **The Olefins.**—The unsaturated hydrocarbons which contain one carbon-carbon double bond are called *olefins*, and have general formula C_nH_{2n}. Ethylene, $CH_2{=}CH_2$ being the simplest olefin, the carbon-carbon double bond is often called the *olefinic bond* or *ethylenic bond*. The series has recently become very important technically, since large quantities of olefins are obtained during cracking of petroleum and may be used to prepare a large variety of organic compounds.

2. **Nomenclature.**—The olefins are named after the corresponding paraffins by changing the suffix *-ane* into *-ylene* in the trivial system, and into *-ene* in the IUPAC system. Thus the series is named as alkylene or alkene series. The longest carbon chain containing the double bond is chosen as the parent alkene and the positions of the double bond and side-chains are indicated by numbers. The lowest possible number is given to the double bond and the side-chains indicated accordingly. Complicated alkenes cannot be named in the trivial system. They are always named according to the IUPAC system. The name of the first few homologues are given below :

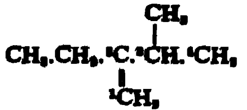
Formula of the olefin	*Corresponding paraffin*	*Common name*	*IUPAC name*
C_nH_{2n}	C_nH_{2n+2} (*alkane*)	Alkylene	Alkene
CH_2	CH_4 (*methane*)	Methylene	Methene
$CH_2{=}CH_2$	C_2H_6 (*ethane*)	Ethylene	Ethene
$CH_3.CH{=}CH_2$	C_3H_8 (*propane*)	Propylene	Propene
$CH_3.CH_2.CH{=}CH_2$	C_4H_{10} (*butane*)	α-Butylene or 1-Butylene	1-Butene
$CH_3.CH{=}CH.CH_3$	,,	β-Butylene or 2-Butylene	2-Butene

The number indicating the position of the double bond is placed before the name. For example, *Formula of the alkene* | *IUPAC-name*



$$^1CH_3.{}^2CH{=}{}^3C{-}{}^4C{-}{}^5CH_3 \quad (^4C\text{ bears }CH_3\text{ above; }{}^3C, {}^4C\text{ bear }CH_3\text{ below})$$

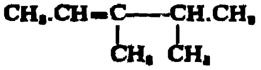
3, 4, 4-Trimethyl-2-pentene



$$CH_3.CH_2.{}^2C.{}^3CH.{}^4CH_3 \quad (\overset{CH_3}{|}\text{ on }{}^3C;\ {}^2C{=}{}^1CH_2)$$

2-ethyl-3-methyl-1-butene

The old practice of denoting the double bond by the Greek letter △ is still continued. The number placed at the upper right-hand corner of the symbol indicates the position of the double bond. For example,



$$CH_3.CH{=}\underset{CH_3}{C}{-}\underset{CH_3}{CH}.CH_3$$

is 3, 4-Dimethyl-Δ^2-pentene *or* 3, 4-Dimethyl-2-pentene

In another method of nomenclature olefins are named as substituted ethylenes. Dialkyl derivatives show isomerism. These are called *symmetrical* (*sym*- or *s*-) when the two alkyl groups are attached to different carbon atoms. These are termed unsymmetrical or asymmetrical (*unsym*- or *as*-) when the two alkyl groups are attached to the same carbon atom. For example,

$CH_3.CH{=}CH.CH_3$	$(CH_3)_2C{=}CH_2$	$(CH_3)_2C{=}CH.CH_3$
s-Dimethylethylene	*as*-Dimethylethylene	Trimethylethylene

3. General Methods of Preparation.—Following are the general methods used for the preparation of olefins :

(*i*) *By dehydration of alcohols.* Primary alcohols when heated with concentrated sulphuric acid at 275-345K, lose a molecule of water to form olefins, *e.g.*, ethanol gives ethylene.

$$\underset{\text{Ethanol}}{C_2H_5OH} \xrightarrow[\text{conc. }H_2SO_4\text{ at }270\text{-}340K]{-H_2O} \underset{\text{Ethylene}}{C_2H_4} \qquad (f.g.)$$

Instead of sulphuric acid, glacial phosphoric acid (HPO_3), phosphorus pentoxide or alumina may be used as dehydrating agent. With alumina at 620K the yields are *v.g.-ex.*

Dehydration of secondary and tertiary alcohols is best carried out using dilute sulphuric acid and the yields are very good. In case concentrated acid is used, the olefins obtained (especially from tertiary alcohols) tend to polymerise.

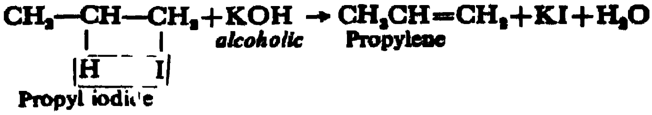
$$\underset{n\text{-Butyl alcohol}}{CH_3.CH_2.CH_2.CH_2OH} \xrightarrow[410K]{75\%H_2SO_4} \underset{\text{2-Butene (\textit{chief product})}}{CH_3.CH{=}CH.CH_3}$$

$$\underset{sec\text{-Butyl alcohol}}{CH_3CH_2CHOH.CH_3} \xrightarrow[370K]{60\%HSO_4} \underset{\text{2-Butene (\textit{chief product})}}{CH_3CH{=}CH.CH_3}$$

$$\underset{tert\text{-Butyl alcohol}}{(CH_3)_2COH.CH_3} \xrightarrow[360\text{-}365K]{20\%H_2SO_4} \underset{\text{Isobutylene}}{(CH_3)_2C{=}CH_2}$$

The formation of 2-butene from *n*-butyl alcohol illustrates a characteristic of dehydration—*the double bond can be formed at a position remote from the carbon originally holding the —OH group.* This characteristic is accounted for due to rearrangement of carbocation to form a stabler one (see page 1.154).

(*ii*) *By the action of alcoholic potash on alkyl halides*, **Dehydrohalogenation**, *e.g.*, propylene from propyl iodide when the yield is about 36 per cent.



$$\underset{\text{Propyl iodide}}{CH_3-\underset{\boxed{H}}{\underset{|}{CH}}-\underset{\boxed{I}}{\underset{|}{CH_2}}}+\underset{\textit{alcoholic}}{KOH} \rightarrow \underset{\text{Propylene}}{CH_3CH=CH_2}+KI+H_2O$$

According to **Saytzeff's Rule**, when two olefins may be formed by dehydrohalogenation of an alkyl halide, the one which is the most substituted olefin predominates. For example, in the dehydrohalogenation of 2-bromobutane,

$$CH_3.CHBr.CH_2.CH_3 \xrightarrow[\text{alc.}]{KOH} \underset{\substack{\text{Dimethylethylene (80\%)}\\ \textit{(Disubstituted)}}}{CH_3.CH=CH.CH_3} \quad ...(1)$$

$$\underset{\substack{\text{Ethylethylene (20\%)}\\ \textit{(Monosubstituted)}}}{CH_2=CH.CH_2CH_3} \quad ...(2)$$

(1) being disubstituted ethylene predominates.

Ease of formation of alkenes :

$$R_2C=CR_2 > R_2C=CHR > R_2C=CH_2,\ RCH=CHR > RCH=CH_2$$

This is also the order of **Stability of alkenes**. Hence **in dehydrohalogenation, more stable the alkene the more easily it is formed**.

In alkyl halides as we proceed from 1° to 2° to 3°, the carbon atom carrying the halogen becomes more and more branched. This increased branching favours dehydrohalogenation in two ways :

(*i*) It provides a greater number of hydrogen atoms for attack by base (See mechanism on page 1·158)and hence a more favourable probability factor towards elimination.

(*ii*) It leads to highly branched (more stable) alkene and hence a more stable transition state and lower value of E_{act}.

As a result of the combined effect of these two factors, **in dehydrohalogenation the order of reactivity of RX is**

$$3° > 2° > 1°.$$

For example, yield of propylene from *iso*propyl halides is up to 80 per cent and that of *iso*-butylene from tertiary butyl halide is 100 per cent. *Ethylene cannot be prepared by this method from ethyl halide* as the yield under most favourable conditions is not more than 1 per cent.

This is not a very important method for the preparation of lower alkenes which can be readily obtained from easily available corresponding alcohols.

On account of the greater certainty as to where the double bond will appear dehydrohalogenation is often preferred over dehydration of alcohols.

(*iii*) *By the action of zinc dust on methanolic solution of a dihalide* (**Dehalogenation**), *e.g.*, propylene from propylene bromide or propylidene bromide.

$$\underset{\text{Propylene bromide}}{CH_3CHBr.CH_2Br} + Zn \rightarrow \underset{\text{Propylene}}{CH_3.CH=CH_2} + ZnBr_2$$

$$\underset{\text{Propylidene bromide}}{CH_3CH_2CHBr_2} + Zn \rightarrow \underset{\text{Propylene}}{CH_3CH=CH_2} + ZnBr_2$$

If sodium is used in place of zinc, an ethereal solution of propylidene bromide gives mainly 3-hexene.

$$\underset{\text{Propylidene bromide}}{2CH_3.CH_2.CH\boxed{Br_2 + 4Na}} \xrightarrow[\text{solution}]{\text{Ether}} \underset{\text{3-Hexene}}{CH_3.CH_2.CH=CH.CH_2CH_3}$$

Propylene bromide gives propylene even with metallic sodium although zinc dust is more satisfactory.

(*iv*) **By dehydrogenation** *of alkanes*. On heating an alkane in the presence of a catalyst (*e.g.*, Cr_2O_3 . Al_2O_3 at 770K) it loses hydrogen to give an alkene.

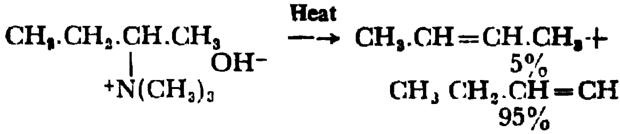
$$\underset{\text{alkane}}{R—CH_2—CH_2—R} \xrightarrow[\text{catalyst}]{\text{Heat}} \underset{\text{alkene}}{R—CH=CH—R}+H_2$$

$$\underset{\text{butane}}{CH_3CH_2.CH_2CH_3} \xrightarrow[770K]{} \underset{\text{2-Butene}}{CH_3CH=CHCH_3} + \text{other butene}$$

(*v*) *By heating quaternary ammonium hydroxide.* For example, tetraethylammonium hydroxide gives ethylene.

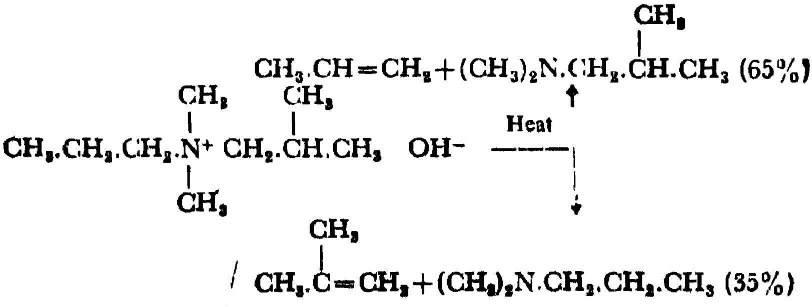
$$(C_2H_5)_4NOH \longrightarrow C_2H_4 + \underset{\text{Triethylamine}}{(C_2H_5)_3N} + H_2O$$

When there are two or more different β-hydrogen atoms in the quaternary ammonium hydroxide, two or more alkenes may be formed. It has been found *that out of the various possible alkenes, the less substituted one is obtained in larger yield* (*cf.* Saytzeff's rule). For example,



$$\underset{\underset{^+N(CH_3)_3}{|}}{CH_3.CH_2.CH.CH_3}\ OH^- \xrightarrow{\text{Heat}} \underset{5\%}{CH_3.CH=CH.CH_3} + \underset{95\%}{CH_3\ CH_2.CH=CH_2}$$

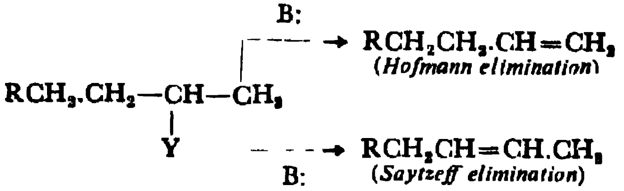
Similar behaviour is noticed in the decomposition of quaternary ammonium compound containing two different alkyl groups resulting in the formation of an alkene. For example,



$$CH_3.CH_2.CH_2.\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N^+}}\ CH_2.\overset{\overset{CH_3}{|}}{C}H.CH_3\ \ OH^- \xrightarrow{\text{Heat}} \begin{cases} CH_3.CH=CH_2+(CH_3)_2N.CH_2.\overset{\overset{CH_3}{|}}{C}H.CH_3 \ (65\%) \\ CH_3.\overset{\overset{CH_3}{|}}{C}=CH_2+(CH_3)_2N.CH_2.CH_2.CH_3 \ (35\%) \end{cases}$$

This mode of elimination is termed **Hofmann rule.**

Orientation in E2 elimination : Saytzeff vs. Hofmann. In the base-induced elimination reaction



where Y = halogen atom, NR_3 or SR_2

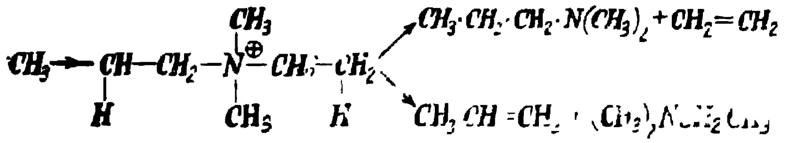
Three factors influencing the relative proportions of the two alkenes produced are :

(*a*) *The relative ease with which the alternative β positions can lose a proton.*

(*b*) *Stability of the alkene produced.* This factor favours Saytzeff elimination.

(*c*) *Size of the leaving group and that of the base.* Bigger size of the leaving group and that of the attacking base favour Hofmann elimination.

In the following elimination


CH_3
$CH_3-CH-CH_2-\overset{\oplus}{N}-CH_2-CH_2$
H
CH_3
H
$CH_3\cdot CH_2\cdot CH_2\cdot N(CH_3)_2+CH_2=CH_2$
$CH_3CH=CH_2$

ethylene is the major product. This is explained in terms of the factor (*a*). Inductive effect of methyl group lowers the acidity of hydrogen attached to β-carbon in propyl group. The hydrogen atom attached to β-carbon atom in ethyl group is, therefore, more acidic and is removed preferentially.

5. General Properties of the Olefins.—

(*a*) **Physical.** Alkenes containing two to four carbon atoms are gases, those containing five to fifteen are liquids and higher ones are solids. They are insoluble in water but soluble in organic solvents and have characteristic smells. These are lighter than water and the lower members act as general anaesthetics. Their physical constants show a regular gradation with the rise of molecular weight.

(*b*) **Chemical.** Important reactions of olefins are :

(1) **Combustion.** They burn with a luminous flame giving carbon dioxide and water vapours and form explosive mixtures with air or oxygen.

$$C_2H_4+3O_2 \rightarrow 2CO_2+2H_2O$$

(2) **Electrophilic Addition reactions.** As a carbon-carbon double bond consists of a strong σ bond plus a weaker π bond as

shown in Fig. 14·1. The π electrons are loosely held between the carbon nuclei and are, therefore, readily polarisable. Addition to compound containing a carbon-carbon double bond involves breaking of the π bond. Bond fission may be heterolytic and the addition proceeds through ionic mechanism. Bond fission may also be homolytic resulting in the formation of diradical addition to which takes place by free radical mechanism.

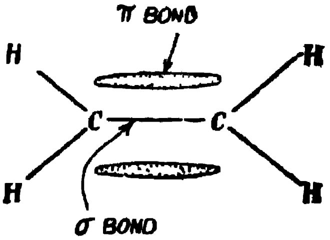
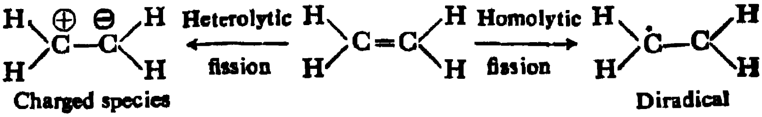
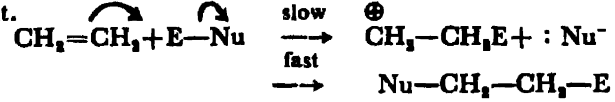


Fig. 14·1—σ and π bonds constitute a double bond.



In polar solvents, addition proceeds predominantly by ionic mechanism whereas in presence of light or free radicals it follows free radical mechanism. The loosely held π electrons are particularly available to an electrophilic reagent (an acidic reagent seeking a pair of electrons). One typical reaction of alkenes is, therefore, electrophilic addition.

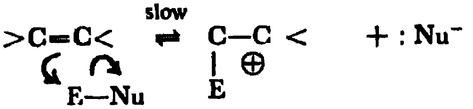
In the addition of an electrophilic reagent across the double bond two new σ-bonds are formed. These are formed at the expense of the destruction or opening of the π bond and the bond in the reagent.



$$CH_2{=}CH_2 + E{-}Nu \xrightarrow{\text{slow}} \overset{\oplus}{C}H_2{-}CH_2E + :Nu^- \xrightarrow{\text{fast}} Nu{-}CH_2{-}CH_2{-}E$$

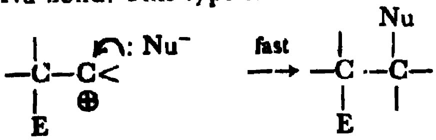
Electrophilic addition occurs in two steps :

(1) The electrophile E attacks the π electrons of the alkene, forming C—E bond and a carbocation.



$$>C{=}C< \;\xrightleftharpoons{\text{slow}}\; \underset{E}{\underset{|}{C}}{-}\overset{\oplus}{C}< \;+ :Nu^- \qquad E{-}Nu$$

(2) In the second step nucleophile (: Nu⁻) attacks the carbocation from the side opposite the C—E bond to form a new C—Nu bond. This type of addition is referred to as *trans*-addition.



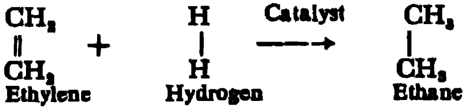
$$-\underset{E}{\overset{|}{\underset{|}{C}}}-\overset{\oplus}{C}< \;\; :Nu^- \xrightarrow{\text{fast}} -\underset{E}{\overset{|}{\underset{|}{C}}}-\underset{|}{\overset{Nu}{\overset{|}{C}}}-$$

The first step (addition of electrophile) being slow is the rate-determining step, the addition reaction is, therefore, termed electrophilic addition.

Free radicals seek an electron each and we see that alkenes also undergo **free radical addition.**

The following examples will illustrate the process :

(*i*) ADDITION OF HYDROGEN. In the presence of a catalyst, ethylene combines with *hydrogen gas* under pressure to give ethane.

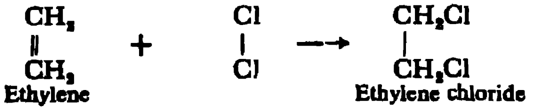


$$\begin{array}{ccccc} CH_2 & & H & \text{Catalyst} & CH_3 \\ \| & + & | & \longrightarrow & | \\ CH_2 & & H & & CH_3 \\ \text{Ethylene} & & \text{Hydrogen} & & \text{Ethane} \end{array}$$

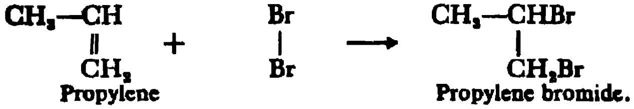
Finely divided platinum and palladium[*] are effective catalysts at room temperature. Supported nickel[†] (Sabatier-Senderens reduction) requires a temperature between 470-570K. Raney nickel[‡] is effective at room temperature and atmospheric pressure.

Hydrogenation of alkenes is a *cis* addition. It is a *free-radical addition* reaction as explained on page 1·165.

(*ii*) ADDITION OF HALOGENS. With halogens, alkenes form the dihalides. The order of reactivity is chlorine $>$ bromine $>$ iodine.



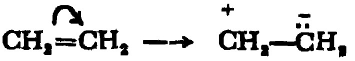
$$\begin{array}{ccccc} CH_2 & & Cl & & CH_2Cl \\ \| & + & | & \longrightarrow & | \\ CH_2 & & Cl & & CH_2Cl \\ \text{Ethylene} & & & & \text{Ethylene chloride} \end{array}$$



$$\begin{array}{ccccc} CH_3-CH & & Br & & CH_3-CHBr \\ \| & + & | & \longrightarrow & | \\ CH_2 & & Br & & CH_2Br \\ \text{Propylene} & & & & \text{Propylene bromide.} \end{array}$$

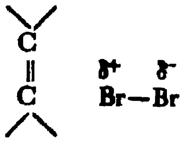
Decolorisation of 5% solution of bromine in carbon tetrachloride is used as a test for alkenes or the double bond.

Electronic Mechanism. The high reactivity of the olefinic bond is due to the presence of two π-electrons which readily undergo electromeric effect at the requirement of the attacking reagent. During addition of bromine, ethylene undergoes electromeric effect.



$$CH_2\overset{\curvearrowright}{=}CH_2 \longrightarrow \overset{+}{C}H_2-\overset{-}{\ddot{C}}H_2$$

A halogen molecule is non-polar. In the vicinity of a dense electron cloud of the carbon-carbon double bond, however, it gets polarised.



Polarisation of Br_2 by a double bond

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[*] Finely divided platinum and palladium commonly known as platinum and palladium black may be prepared by reducing their soluble salts with formaldehyde.

[†] To get Supported nickel some suitable porous material, *e.g.*, kieselguhr, is impregnated with a nickel salt and treated with sodium hydroxide. It is then washed and dried. The resulting nickel oxide is reduced with hydrogen at 670-720K. Finely divided particles suspended in the porous material are obtained.

[‡] To prepare Raney nickel digest an alloy containing equal amounts of nickel and aluminium with sodium hydroxide. The aluminium is dissolved away and the residue of finely divided nickel is washed and stored under water and ethanol, etc.

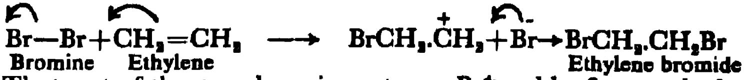
The polarised bromine molecule approaches the ethylene molecule forming the transition complex which then breaks as given below :

$$\underset{\text{Transition complex}}{\overset{\delta^-}{Br}\ldots\overset{\delta^+}{Br}\ldots\ddot{C}H_2-\overset{+}{C}H_2} \longrightarrow \overset{-}{Br}+Br-CH_2-\overset{+}{C}H_2$$

Next, the bromide ion attaches to the positively charged carbon atom.

$$Br-CH_2-\overset{+}{C}H_2+Br^- \longrightarrow \underset{\text{Ethylene bromide}}{Br-CH_2-CH_2-Br}$$

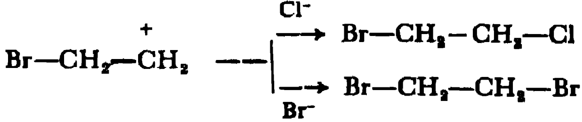
Combining the equations we can represent the addition as :



$$\underset{\text{Bromine}}{Br-Br}+\underset{\text{Ethylene}}{CH_2=CH_2} \longrightarrow BrCH_2.\overset{+}{C}H_2+Br^- \rightarrow \underset{\text{Ethylene bromide}}{BrCH_2.CH_2Br}$$

That out of the two bromine atoms Br^+ adds first and the addition of Br^- takes place next is supported by the formation of a mixture of CH_2Br-CH_2Cl and CH_2Br-CH_2Br when ethylene is treated with bromine water containing sodium chloride. This is because both Br^- and Cl^- ions are available in the second step and both of them compete for the positively charged carbon atom in

$Br-CH_2-\overset{+}{C}H_2$.



It is a *trans addition* taking place *via* the formation of intermediate product, carbocation or bromonium ion as explained on page 1·156.

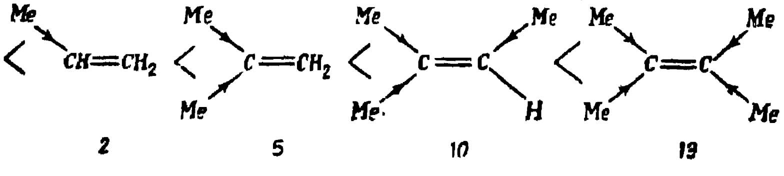
Effect of Substituents on Rate of Addition. Rate determining step in the addition of Br_2 is the attack by incipient electrophile $Br^{\oplus}$ forming carbocation or bromonium ion. It would be expected that presence of electron-donating groups on the carbon atoms bonded through the double bond would facilitate the addition of an electrophile.

On the other hand presence of electron-withdrawing groups would slow down the rate of addition.

This has actually been observed in practice. For example, rate of addition increases with successive replacement of hydrogen atoms by electron-releasing methyl groups and decreases when hydrogen is replaced by electron-withdrawing groups like Br and COOH.

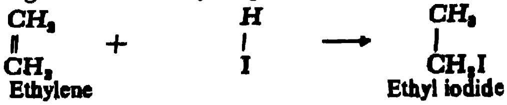
The relative rates of addition are observed in the following order :

$$\underset{0.03}{CH_2=CH\rightarrow Br \approx CH_2=CH\rightarrow COOH} < \underset{1}{CH_2=CH_2}$$



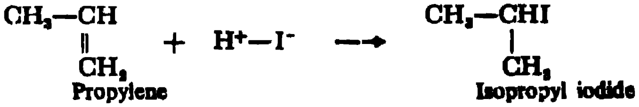
(*iii*) ADDITION OF HALOGEN ACIDS. Alkenes react with strong aqueous solution of *halogen acids* to give alkyl halides. The order of reactivity is :

hydrogen iodide > hydrogen bromide > hydrogen chloride.



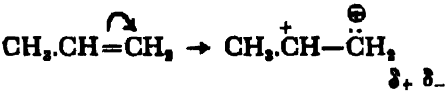
$$\underset{\text{Ethylene}}{\begin{array}{c}CH_2\\ \|\\ CH_2\end{array}} + \begin{array}{c}H\\ |\\ I\end{array} \longrightarrow \underset{\text{Ethyl iodide}}{\begin{array}{c}CH_3\\ |\\ CH_2I\end{array}}$$

Markownikoff studied many reactions of this kind and formulated the rule called **Markownikoff's Rule** : *The negative part of the addendum (molecule to be added) adds on to the less hydrogenated (more substituted) carbon atom.* For example, isopropyl iodide is obtained by adding hydriodic acid to propylene.



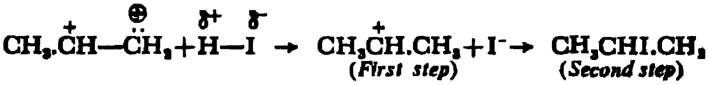
$$\underset{\text{Propylene}}{\begin{array}{l}CH_3{-}CH\\ \qquad\ \|\\ \qquad CH_2\end{array}} + H^+{-}I^- \longrightarrow \underset{\text{Isopropyl iodide}}{\begin{array}{l}CH_3{-}CHI\\ \qquad\ \ |\\ \qquad CH_3\end{array}}$$

Electronic mechanism. In the addition of hydrogen iodide to propylene as the methyl group is electron repelling, the electromeric effect takes place as under :



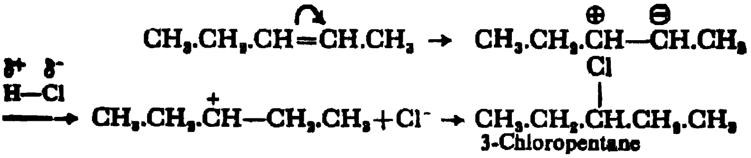
$$CH_3.CH{=}CH_2 \rightarrow CH_3.\overset{+}{C}H-\underset{\delta+\ \delta-}{\overset{\ominus}{\ddot{C}H_2}}$$

To this a polarised molecule of hydriodic acid (H—I) adds in two steps as given below :



$$CH_3.\overset{+}{C}H-\overset{\ominus}{\ddot{C}}H_2+\overset{\delta+}{H}-\overset{\delta-}{I} \rightarrow \underset{(\textit{First step})}{CH_3\overset{+}{C}H.CH_3}+I^- \rightarrow \underset{(\textit{Second step})}{CH_3CHI.CH_3}$$

In 2-pentene, $CH_3.CH_2.CH{=}CH.CH_3$, the C_2H_5 group is more electron repelling than the CH_3 group, hence addition of HCl takes place as follows giving chiefly 3-chloropentane.



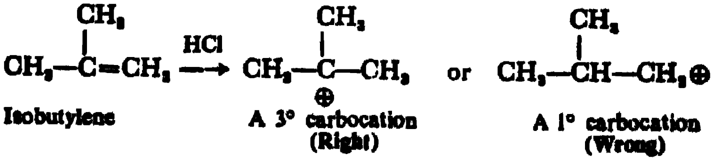
$$CH_3.CH_2.CH{=}CH.CH_3 \rightarrow CH_3.CH_2.\overset{\oplus}{C}H-\overset{\ominus}{C}H.CH_3$$

$$\xrightarrow{\overset{\delta+}{H}-\overset{\delta-}{Cl}} CH_3.CH_2.\overset{+}{C}H-CH_2.CH_3+Cl^- \rightarrow \underset{\text{3-Chloropentane}}{CH_3.CH_2.\overset{\begin{array}{c}Cl\\ |\end{array}}{C}H.CH_2.CH_3}$$

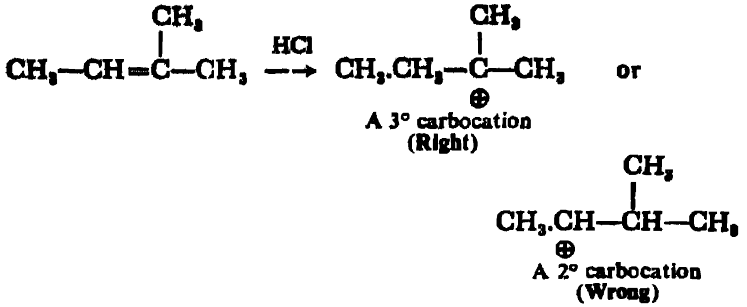
Markownikoff's rule has now been replaced by a more general rule : **electrophilic addition to a carbon-carbon double bond involves the intermediate formation of a more stable carbocation**, their order of stability being

$$3° > 2° > 1° > CH_3\oplus$$

For example, first step in the addition of HCl to the following alkenes is :



$$\underset{\text{Isobutylene}}{CH_3-\overset{\begin{array}{c}CH_3\\ |\end{array}}{C}{=}CH_2} \xrightarrow{HCl} \underset{\begin{array}{c}\text{A 3° carbocation}\\ \text{(Right)}\end{array}}{CH_3-\underset{\oplus}{\overset{\begin{array}{c}CH_3\\ |\end{array}}{C}}-CH_3} \quad \text{or} \quad \underset{\begin{array}{c}\text{A 1° carbocation}\\ \text{(Wrong)}\end{array}}{CH_3-\overset{\begin{array}{c}CH_3\\ |\end{array}}{C}H-CH_2\oplus}$$



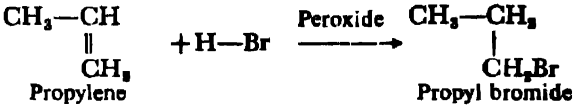
$$CH_3-CH=\overset{\displaystyle CH_3}{\overset{|}{C}}-CH_3 \xrightarrow{HCl} CH_3.CH_2-\underset{\oplus}{\overset{\displaystyle CH_3}{\overset{|}{C}}}-CH_3 \quad \text{or}$$

A 3° carbocation
(Right)

$$CH_3.\underset{\oplus}{CH}-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_3$$

A 2° carbocation
(Wrong)

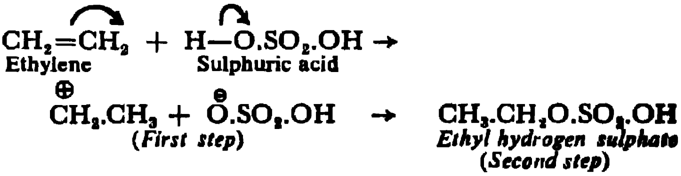
In the presence of air or peroxides that are formed when alkene remains exposed to air or added peroxides, addition of hydrogen bromide is abnormal as it takes place against the Markownikoff's rule. The action of peroxide to cause this abnormal addition is termed **Peroxide Effect.**



$$\underset{\text{Propylene}}{\begin{matrix}CH_3-CH\\ \quad\ \ \| \\ \quad\ \ CH_2\end{matrix}} + H-Br \xrightarrow{\text{Peroxide}} \underset{\text{Propyl bromide}}{\begin{matrix}CH_3-CH_2\\ \quad\quad | \\ \quad\quad CH_2Br\end{matrix}}$$

The mechanism of the peroxide effect is given on page 1·164.

(*iv*) ADDITION OF SULPHURIC ACID. Ethylene is readily absorbed by *concentrated sulphuric aid*, and still better by fuming sulphuric acid to produce ethyl hydrogen sulphate



$$\underset{\text{Ethylene}}{CH_2=CH_2} + \underset{\text{Sulphuric acid}}{H-O.SO_2.OH} \rightarrow$$

$$\underset{(\textit{First step})}{\overset{\oplus}{C}H_2.CH_3 + \overset{\ominus}{O}.SO_2.OH} \rightarrow \underset{\substack{\textit{Ethyl hydrogen sulphate}\\(\textit{Second step})}}{CH_3.CH_2O.SO_2.OH}$$

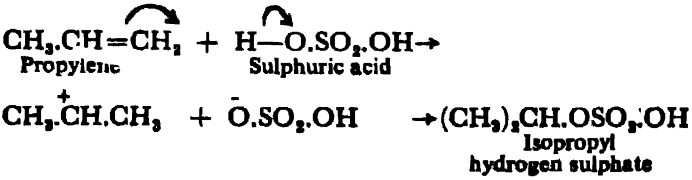
Ethyl hydrogen sulphate gives ethylene when heated to 430-440K while ethanol is obtained on boiling it with water.

$$\underset{\text{Ethyl hydrogen sulphate}}{C_2H_5OSO_3H} \xrightarrow{\text{Heat}} \underset{\text{Ethylene}}{C_2H_4} + \underset{\text{Sulphuric acid}}{H_2SO_4}$$

$$C_2H_5\boxed{OSO_3H+H}OH \rightarrow \underset{\text{Ethyl alcohol}}{C_2H_5OH} + H_2SO_4$$

The reaction is, therefore, used in the separation of ethylene from a gaseous mixture and production of ethanol starting with ethylene.

Addition of sulphuric acid to higher alkenes takes place according to Markownikoff's rule.



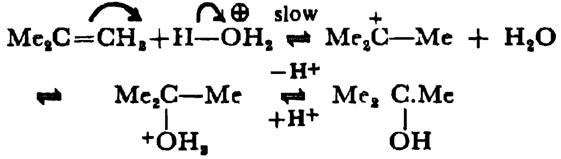
$$\underset{\text{Propylene}}{CH_3.CH=CH_2} + \underset{\text{Sulphuric acid}}{H-O.SO_2.OH} \rightarrow$$

$$CH_3.\overset{+}{C}H.CH_3 + \overset{-}{O}.SO_2.OH \rightarrow \underset{\substack{\text{Isopropyl}\\ \text{hydrogen sulphate}}}{(CH_3)_2CH.OSO_2.OH}$$

(*v*) HYDRATION OF OLEFINS. Olefins may be hydrated to alcohols by absorption in concentrated sulphuric acid followed by hydrolysis of alkyl sulphate as given above. They may, however, be catalytically hydrated in dilute acid solution, *e.g.*, isobutylene gives *tert*-butyl alcohol in dilute acid solution.

$$(CH_3)_2C{=}CH_2 + H_2O \xrightarrow{H^+} (CH_3)_3COH$$

The mechanism of reaction is not yet settled. Hughes and Ingold have proposed the following mechanism :



$$Me_2C{=}CH_2 + H{-}\overset{\oplus}{O}H_2 \underset{}{\overset{\text{slow}}{\rightleftharpoons}} Me_2\overset{+}{C}{-}Me + H_2O$$

$$\rightleftharpoons \underset{{}^{+}OH_2}{Me_2C{-}Me} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} \underset{OH}{Me_2\,C.Me}$$

The first step is protonation to form a carbocation and being slow is the rate determining step. The second step is addition of water to the carbocation followed by the loss of proton by the addition compound.

(*vi*) HYDROBORATION (*Hydroboronation*). With diborane, $(BH_3)_2$ alkenes undergo addition reaction (Hydroboration) to yield alkylboranes, R_3B which on oxidation give alcohols. For example,

$$BH_3 \xrightarrow{CH_2=CH_2} CH_3CH_2BH_2 \xrightarrow{CH_2=CH_2} (CH_3CH_2)_2BH$$

$$\xrightarrow{CH_2=CH_2} \underset{\text{Triethylborane}}{(CH_3CH_2)_3B}$$

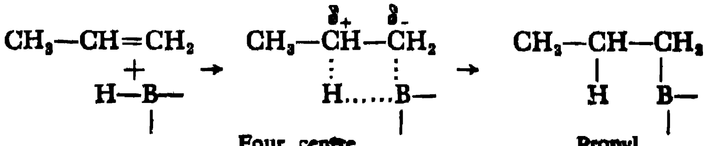
$$(CH_3CH_2)_3B + 3H_2O_2 \xrightarrow{OH^-} 3CH_3CH_2OH + H_3BO_3$$

The overall process is equivalent to the **anti-Markownikoff hydration** of an olefin although actual addition of diborane to olefin does obey Markownikoff's rule. *Borane is an electron-deficient molecule and, therefore, behaves as an electrophile which attacks at a point of highest electron density.*

$$\underset{\text{Propene}}{CH_3.CH{=}CH_2} \xrightarrow{(BH_3)_2} \xrightarrow[(-H_3BO_3)]{H_2O_2,\ NaOH} \underset{\text{1-Propanol}}{CH_3.CH_2CH_2OH}$$

Mechanism of Hydroboration. Diborane $(BH_3)_2$ acts as if it were in the monomeric form, BH_3 (Borane). Borane adds successively to double bonds of three molecules of alkenes until all the hydrogens are replaced by alkyl groups. In each addition step the boron atom attaches to the least substituted carbon of the double bond.

The reaction proceeds *via* the formation of a four-centre transition state.



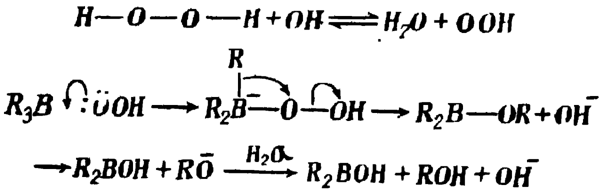
$$\begin{array}{c} CH_3{-}CH{=}CH_2 \\ + \\ H{-}\underset{|}{B}{-} \end{array} \rightarrow \begin{array}{c} CH_3{-}\overset{\delta+}{CH}{-}\overset{\delta-}{CH_2} \\ \vdots \quad\ \vdots \\ H\ldots\ldots\underset{|}{B}{-} \end{array} \rightarrow \begin{array}{c} CH_3{-}CH{-}CH_2 \\ |\qquad | \\ H\qquad \underset{|}{B}{-} \end{array}$$

Four, centre transition state

Propyl borane

In the transition state formation of carbon-boron bond has proceeded to a greater extent than the formation of carbon-hydrogen bond. A partial positive charge, therefore, develops on the secondary carbon atom.

Oxidation of the final addition product of hydroboration with alkaline H_2O_2 is represented as follows :



$$H{-}O{-}O{-}H + \bar{O}H \rightleftharpoons H_2O + \bar{O}OH$$

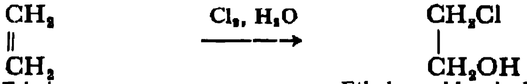
$$R_3B + :\ddot{O}OH \longrightarrow R_2\overset{R}{\underset{|}{\bar{B}}}{-}O{-}OH \longrightarrow R_2B{-}OR + \bar{O}H$$

$$\longrightarrow R_2BOH + R\bar{O} \xrightarrow{H_2O} R_2BOH + ROH + \bar{O}H$$

This step is repeated and the final products are $3ROH + H_3BO_3$

Hydroboration has almost entirely replaced peroxide initiated by hydrobromination reaction which was long used for the same purpose.

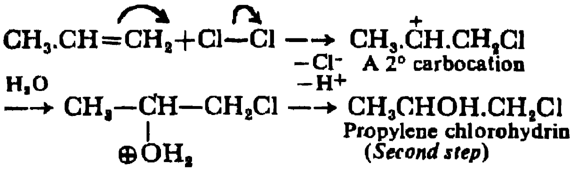
(*vii*) ADDITION OF HYPOHALOUS ACID. Ethylene forms ethylene halohydrin with chlorine or bromine in the presence of water.



$$CH_2{=}CH_2 \xrightarrow{Cl_2,\ H_2O} CH_2Cl{-}CH_2OH$$

Ethylene Ethylene chlorohydrin

With higher homologues addition takes place according to Markownikoff's rule.



$$CH_3.CH{=}CH_2{+}Cl{-}Cl \longrightarrow CH_3.\overset{+}{C}H.CH_2Cl \quad \text{A } 2^\circ \text{ carbocation}$$

$$\xrightarrow{H_2O} CH_3{-}\underset{\oplus OH_2}{\underset{|}{C}H}{-}CH_2Cl \xrightarrow[-H^+]{} CH_3CHOH.CH_2Cl$$

$-Cl^-$

Propylene chlorohydrin
(*Second step*)

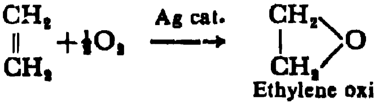
Whatever the mechanism, the result is addition of the elements of hypohalous acid (HO and X) and the reaction is often referred to in that way.

Similarly, a bromohydrin is obtained with Br_2 and H_2O.

$$CH_2{=}CH_2 \xrightarrow{Br_2/H_2O} CH_2Br{-}CH_2OH$$

Ethylene bromohydrin

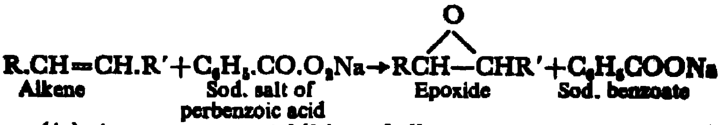
(*viii*) ADDITION OF OXYGEN. Lower alkenes when mixed with air and passed under pressure over a silver catalyst at 470-670K add an atom of oxygen to give alkene *oxides* or *epoxides*.



$$CH_2{=}CH_2 + \tfrac{1}{2}O_2 \xrightarrow{\text{Ag cat.}} (CH_2)_2O$$

Ethylene oxide

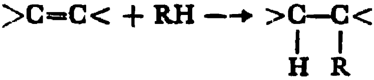
Epoxides are also obtained when alkenes are treated with peracids (*e.g.*, perbenzoic acid).



$$\mathrm{R.CH{=}CH.R' + C_6H_5.CO.O_2Na \rightarrow RCH\overset{O}{—}CHR' + C_6H_5COONa}$$

Alkene Sod. salt of perbenzoic acid Epoxide Sod. benzoate

(*ix*) ALKYLATION. Addition of alkanes can be represented as follows :



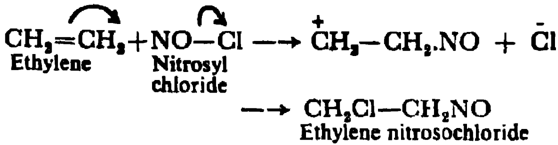
$$>C{=}C< + RH \longrightarrow >\underset{H}{C}{-}\underset{R}{C}<$$

For example, isobutylene and isobutane react in the presence of concentrated sulphuric acid (*catalyst*) to give 2, 2, 4-trimethylpentane (*neo*-octane).

$$\underset{\text{Isobutane}}{(CH_3)_3CH} + \underset{\text{Isobutylene}}{CH_2{=}C(CH_3)_2} \longrightarrow \underset{\substack{\textit{neo}\text{-octane} \\ \text{(2, 2, 4-trimethylpentane)}}}{(CH_3)_3C{-}CH_2{-}CH(CH_3)_2}$$

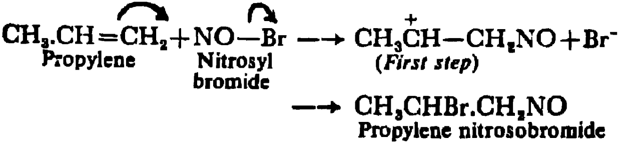
For mechanism of the reaction see page 1·150.

(*x*) ADDITION OF NITROSYL CHLORIDE OR BROMIDE. Nitrosyl halides are obtained



$$\underset{\text{Ethylene}}{CH_2{=}CH_2} + \underset{\text{Nitrosyl chloride}}{NO{-}Cl} \longrightarrow \overset{+}{C}H_2{-}CH_2.NO + \overset{-}{Cl}$$

$$\longrightarrow \underset{\text{Ethylene nitrosochloride}}{CH_2Cl{-}CH_2NO}$$

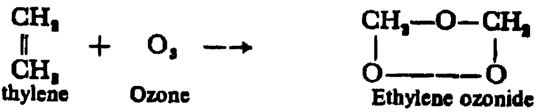


$$\underset{\text{Propylene}}{CH_3.CH{=}CH_2} + \underset{\text{Nitrosyl bromide}}{NO{-}Br} \longrightarrow \underset{\textit{(First step)}}{CH_3\overset{+}{C}H{-}CH_2NO + Br^-}$$

$$\longrightarrow \underset{\text{Propylene nitrosobromide}}{CH_3CHBr.CH_2NO}$$

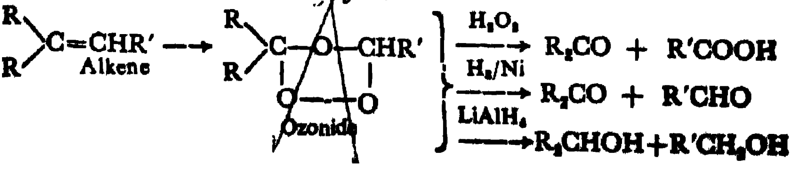
Addition of H—X, H—OSO$_3$H, H—OH, X$_2$, NOX, HOX are all *trans addition reactions.*

(*xi*) ADDITION OF OZONE. On passing a stream of ozonized oxygen through a solution of an olefin in an organic solvent, an *ozonide* is obtained.



Ethylene Ozone Ethylene ozonide

The ozonide on oxidation with H$_2$O$_2$ or peracids gives acids and/or ketones. On reduction with zinc and acid or hydrogen in the presence of a catalyst (Raney nickel) it gives aldehydes and/or ketones. Reduction with LiAlH$_4$ yields corresponding alcohols. The nature of these products helps in locating the position of the double bond in olefin—*Ozonolysis.*



$$\xrightarrow{H_2O_2} R_2CO + R'COOH$$

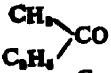
$$\xrightarrow{H_2/Ni} R_2CO + R'CHO$$

$$\xrightarrow{LiAlH_4} R_2CHOH + R'CH_2OH$$

Example 1. *On ozonolysis followed by reduction C_6H_{12}* (A) *gives an aldehyde C_2H_4O* (B) *and a ketone C_4H_8O* (C). *Identify the compounds* A, B *and* C.

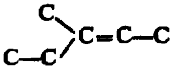
Compound C_2H_4O (B) is an aldehyde and must have the characteristic group of aldehydes (CHO). Hence the only structure that can be assigned to it is $CH_3.CHO$ (*Acetaldehyde*).

Compound C_4H_8O (C) is a ketone and must have the characteristic group of ketone (>CO). Hence the only structure that can be assigned to it is



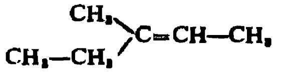
$$\begin{matrix}CH_3\\ C_2H_5\end{matrix}\!\!>CO$$ (*Ethyl methyl ketone*).

Compound C_6H_{12} (A) corresponds to the general formula of the alkenes C_nH_{2n} and is, therefore, an alkene. On ozonolysis followed by hydrolysis the chain breaks at the point of the double bond. The products (C_2H_4O and C_4H_8O) obtained here suggest that there are two carbon atoms on one side of the double bond and four carbon atoms on the other end of the double bond. The two carbon atoms are arranged as in acetaldehyde and the four carbon atoms are arranged as in ethyl methyl ketone. Hence we can assign the following skeleton to the olefin :



$$\begin{matrix}C\\ C-C\end{matrix}\!\!>C=C-C$$

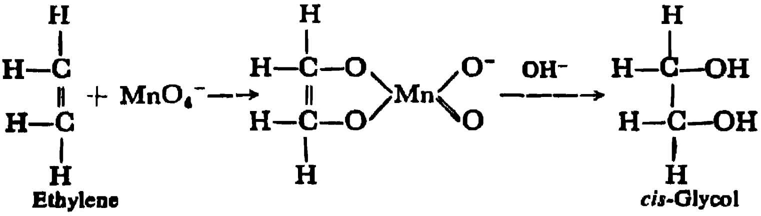
Putting hydrogen atoms to ensure that four valencies of each carbon atom are satisfied, we have the structural formula of A as



$$\begin{matrix}CH_3\\ CH_3-CH_2\end{matrix}\!\!>C=CH-CH_3$$

(3) **Oxidation.** Olefins are readily oxidised, the oxidation products depend upon the nature of oxidising agent used, *e.g.*,

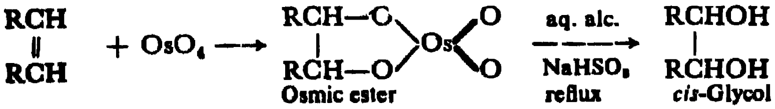
(*a*) *With cold dilute alkaline permanganate solution* (**Baeyer's reagent**), alkenes are converted into dihydroxy compounds called *glycols* and the permanganate solution gets decolorised. It is *cis*-hydroxylation proceeding via a cyclic intermediate (*cf.* OsO_4 below).



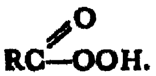
Decolorisation of Baeyer's reagent is also used as a test for olefins or the double bond.

90% hydrogen peroxide in glacial acetic acid also gives glycols.

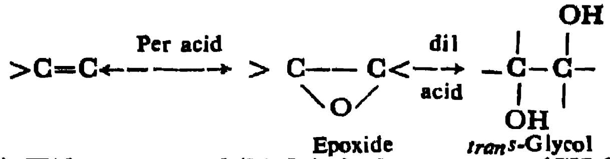
Hydroxylation of olefins may be effected by means of osmium tetroxide which adds at the double bond. The cyclic compound on refluxing with aqueous alcoholic $NaHSO_3$ gives *cis*- glycol.



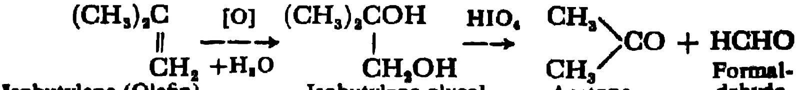
To get a *trans*-glycol oxidation is carried out with a peracid,



$RC(=O)OOH$.

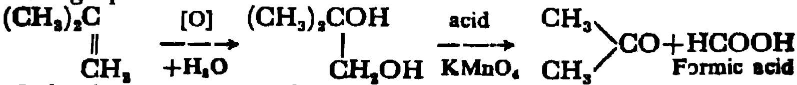


(*b*) *With pe acid* (HIO_4), *lead tetra-acetate*, $(CH_3COO)_4Pb$ or *sodium bismu e*, the glycols produced by hydroxylation of olefins are further oxidised to aldehydes or ketones depending upon the structure of the olefin.



$$\underset{\text{Isobutylene (Olefin)}}{\begin{matrix}(CH_3)_2C\\ \| \\ CH_2\end{matrix}} \xrightarrow[+H_2O]{[O]} \underset{\text{Isobutylene glycol}}{\begin{matrix}(CH_3)_2COH\\ | \\ CH_2OH\end{matrix}} \xrightarrow{HIO_4} \underset{\text{Acetone}}{\begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>CO} + \underset{\text{Formaldehyde}}{HCHO}$$

(*c*) *With acid permanganate or acid dichromate*, the glycol produced by hydroxylation is further oxidised to an acid or ketone depending upon the olefin.



$$\underset{\text{Isobutylene}}{\begin{matrix}(CH_3)_2C\\ \| \\ CH_2\end{matrix}} \xrightarrow[+H_2O]{[O]} \underset{\text{Isobutylene glycol}}{\begin{matrix}(CH_3)_2COH\\ | \\ CH_2OH\end{matrix}} \xrightarrow[KMnO_4]{acid} \underset{\text{Acetone}}{\begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>CO} + \underset{\text{Formic acid}}{HCOOH}$$

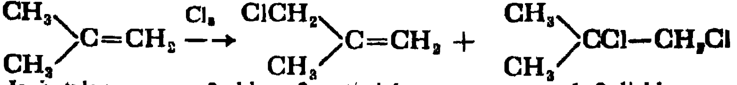
The nature of oxidation products helps us in locating the position of the double bond as in the case of ozonolysis.

(*d*) *Atmospheric oxidation.* Compounds containing double and triple bonds are slowly oxidised by atmospheric oxygen forming gums and waxes due to formation of cross-linked polymers. Drying of oils used in paints and varnishes is as a result of this oxidation. Now we can understand why the presence of unsaturated hydrocarbons in gasoline and lubricants is undesirable.

(675-8(4) **Substitution reactions.** At higher temperatures 75K) olefins give substitution products with chlorine.

$$\underset{\text{Porpylene}}{CH_2{=}CH.CH_3} + Cl_2 \xrightarrow{675\text{-}875K} \underset{\text{Allyl chloride}}{CH_2{=}CH.CH_2Cl} + HCl$$

With branched-chain olefins substitution is fairly easy. For example, isobutylene gives substitution product with chlorine even at room temperature.



$$\underset{\text{Isobutylene}}{\begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>C{=}CH_2} \xrightarrow{Cl_2} \underset{\substack{\text{3-chloro-2-methyl-1-propene}\\ (\textit{Main product})}}{\begin{matrix}ClCH_2\\ CH_3\end{matrix}\!\!>C{=}CH_2} + \underset{\substack{\text{1, 2-dichloro-}\\ \text{2-methylpropane}\\ (\textit{Traces of addition product})}}{\begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>CCl{-}CH_2Cl}$$

Substitution by halogens is a free-radical substitution reaction as shown below :

$$X^{\cdot} + CH_3{-}CH{=}CH_2 \longrightarrow HX + \underset{\text{Allyl radical}}{{}^{\cdot}CH_2{-}CH{=}CH_2}$$

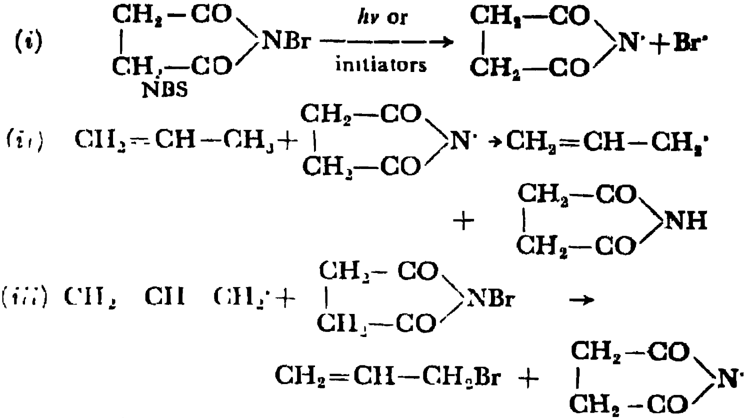
$$\xrightarrow{X_2} \underset{\substack{\text{Allyl halide Actual product at}\\ \text{high temperature or low halogen}\\ \text{concentration. } (X{=}Cl,\ Br)}}{X{-}CH_2{-}CH{=}CH_2} + X^{\cdot}$$

Ease of formation of free radicals is in the order :

$$\text{allyl} > 3^{\circ} > 2^{\circ} > 1^{\circ} > CH_3^{\cdot} > \text{vinyl}$$

This type of reaction involving substitution at the alpha carbon atom with respect to the double bond is termed **Allylic substitution.**

N-Bromosuccinimide (NBS) is an important reagent used for allylic bromination.



$$(i)\quad \underset{\text{NBS}}{\begin{array}{l} CH_2-CO \\ | \\ CH_2-CO \end{array}\!\!>NBr} \xrightarrow[\text{initiators}]{h\nu \text{ or}} \begin{array}{l} CH_2-CO \\ | \\ CH_2-CO \end{array}\!\!>N^{\cdot}+Br^{\cdot}$$

$$(ii)\quad CH_2=CH-CH_3+\begin{array}{l} CH_2-CO \\ | \\ CH_2-CO \end{array}\!\!>N^{\cdot} \rightarrow CH_2=CH-CH_2^{\cdot} + \begin{array}{l} CH_2-CO \\ | \\ CH_2-CO \end{array}\!\!>NH$$

$$(iii)\quad CH_2=CH-CH_2^{\cdot}+\begin{array}{l} CH_2-CO \\ | \\ CH_2-CO \end{array}\!\!>NBr \rightarrow CH_2=CH-CH_2Br + \begin{array}{l} CH_2-CO \\ | \\ CH_2-CO \end{array}\!\!>N^{\cdot}$$

Step (*i*) is the chain initiating step whereas steps (*ii*) and (*iii*) are chain-propagating steps.

(5) **Isomerisation.** Olefins undergo isomerisation when heated alone at 770-970K or when heated in the presence of catalysts, *e.g.*, $Al_2(SO_4)_3$ 470-570K. Isomerisation may be due to

(*a*) *Either* shifting of double bond which always tends to move towards the centre of the chain, *e.g.*,

$$\underset{\text{1-Pentene}}{CH_3.CH_2.CH_2.CH=CH_2} \longrightarrow \underset{\text{2-Pentene}}{CH_3.CH_2.CH=CH.CH_3}$$

(*b*) *Or* migration of a methyl group, *e.g.*,

$$\underset{\text{1-Butene}}{CH_3.CH_2.CH=CH_2} \longrightarrow \underset{\text{Isobutylene}}{(CH_3)_2C=CH_2}$$

Both of these changes might occur simultaneously in some cases.

(6) **Polymerisation.** Olefins polymerise in presence of suitable catalyst, *e.g.*,

$$\underset{\text{Ethylene}}{nCH_2=CH_2} \xrightarrow[\text{high pressure}]{\text{High temp. \&}} \underset{\text{Polyethylene}}{(C_2H_4)_n} \text{ or } \underset{\text{or Polythene}}{-(-CH_2-CH_2-)_n-}$$

$$\underset{\text{Isobutylene}}{nC_4H_8} \xrightarrow{\text{Conc. } H_2SO_4} \underset{\text{Polymer}}{(C_4H_8)_n}$$

When two compounds have the same empirical formula but differ in molecular weight, the more complicated compound is called the **Polymer** *of the smaller one. The process of formation of a polymer from a simpler compound is termed* **Polymerisation.**

For mechanism of polymerisation see page 1·158.

Tests. (*a*) Alkenes decolorise bromine in CCl_4 without evolution of HBr. (This test is also given by alkynes.)

(*b*) They decolorise alkaline $KMnO_4$ (Baeyer's reagent). This test is given by alkynes and aldehydes.

(*c*) They dissolve in cold conc. H_2SO_4. Alcohols and ethers also dissolve in this reagent but alkanes and alkyl halides are not soluble.

(*d*) It can be distinguished from alcohols by the fact that primary and secondary alcohols are oxidised by CrO_3 in aq. H_2SO_4 within two seconds changing clear orange solution opaque blue-green. Tertiary alcohols and alkenes are not affected by CrO_3.

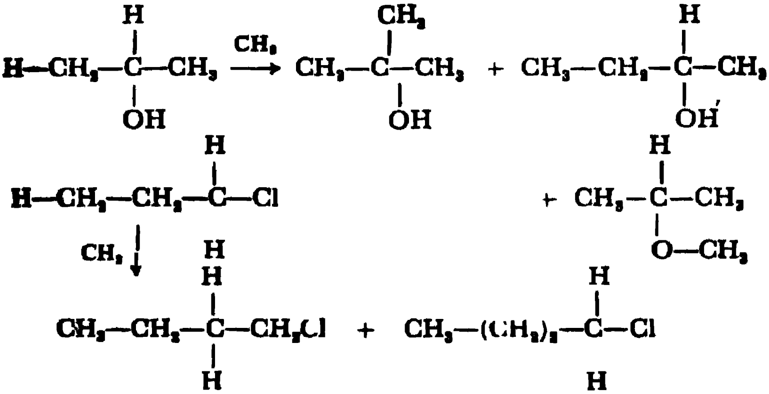
SOME INDIVIDUAL MEMBERS

6. **Methylene (Carbene), CH_2.**—The first member of the olefin series is methylene, CH_2. It is a short-lived bivalent carbon compound. It is formed by the photolysis (photochemical decomposition) or pyrolysis of diazomethane or keten.

$$CH_2N_2 \rightarrow CH_2 + N_2$$
$$CH_2{=}C{=}O \rightarrow CH_2 + CO$$

It is highly reactive and undergoes the following two types of reactions :

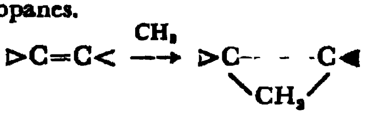
(*i*) **Insertion reactions.** Methylene gets inserted mainly in the C—H bond but insertion can also occur in O—H and C—Cl bonds.



$$H-CH_2-\underset{OH}{\overset{H}{C}}-CH_3 \xrightarrow{CH_2} CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_3 + CH_3-CH_2-\underset{OH}{\overset{H}{C}}-CH_3 + CH_3-\underset{O-CH_3}{\overset{H}{C}}-CH_3$$

$$H-CH_2-CH_2-\underset{H}{\overset{H}{C}}-Cl \xrightarrow{CH_2} CH_3-CH_2-\underset{H}{\overset{H}{C}}-CH_2Cl + CH_3-(CH_2)_2-\underset{H}{\overset{H}{C}}-Cl$$

(*ii*) **Addition reactions.** Methylene adds across a double bond to form cyclopropanes.



$$>C{=}C< \xrightarrow{CH_2} >C\!-\!-\!-\!C< \text{ (bridged by } CH_2)$$

It has been found that methylene exists in two different forms :

(*a*) *Singlet methylene* in which carbon atom is sp^2 hybridised with two electrons in each of these three orbitals.

(*b*) *Triplet methylene* in which carbon atom is sp hybridised with two electrons in each of these two hybridised orbitals and one electron in each of the remaining two p orbitals. It is a diradical.

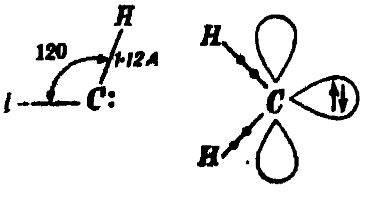


Fig. 14·2(*a*)—Singlet methylene, with unshared electrons paired.

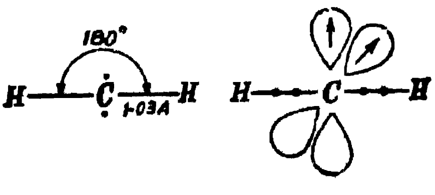


Fig. 14·2(*b*)—Triplet methylene with unshared electrons not paired.

7. Ethylene or Ethene, C_2H_4.—Ethylene occurs in coal gas to the extent of 6% by volume and is the major cause of luminosity of coal gas flame. It is present in the natural gas that issues out from oil-fields. Gaseous mixture produced by cracking of high b.p. oil fractions contains a high percentage of this gas. It is one of the products of destructive distillation of many organic substances.

Preparation of Ethylene. Ethylene may be prepared by any of the general methods of preparation of olefins (except 2). Different methods employed are :

(*i*) Ethylene is most conveniently prepared in the laboratory by heating *ethanol with concentrated sulphuric acid at 430-440K.*

$$C_2H_5OH + H_2SO_4 \xrightarrow[430\text{-}440K]{} C_2H_5HSO_4 + H_2O$$

$$\underset{\text{Ethyl hydrogen sulphate}}{C_2H_5HSO_4} \longrightarrow \underset{\text{Ethylene}}{C_2H_4} + H_2SO_4$$

Expt. 1. Take a mixture of ethanol and 2½ times its volume of concentrated sulphuric acid in a large round-bottom flask (Fig. 14·3) fitted with a dropping funnel, a delivery tube and a thermometer which dips in the mixture. Heat the flask on a sand bath and drop a mixture of equal volumes of ethanol and concentrated sulphuric acid from the dropping funnel. Add a little sand and anhydrous aluminium sulphate to the flask to prevent frothing. The reaction takes place in two stages given above.

A steady current of ethylene gas is evolved. It is contaminated with some sulphur dioxide and carbon dioxide (produced by reduction of sulphuric acid and oxidation of ethanol). The gas evolved is, therefore, passed through a bottle containing caustic soda which removes carbon dioxide and sulphur dioxide present. The purified gas is collected over water as shown in the diagram.

Although the sulphuric acid acts catalytically yet some acid is always lost in the reaction as a result of reduction, etc. After some time, it becomes too dilute to behave as a dehydrating agent.

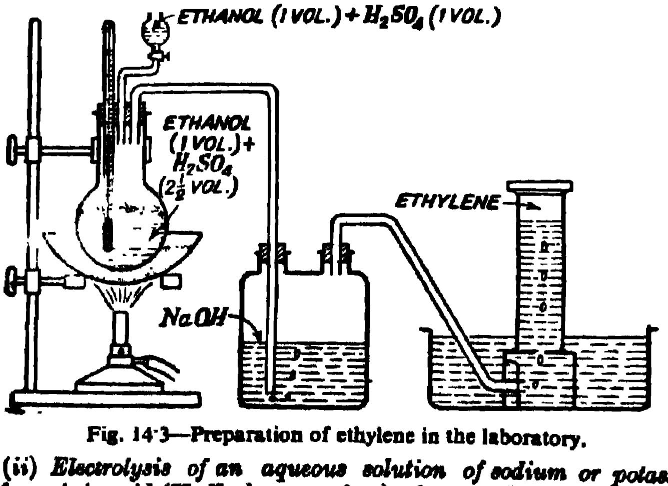
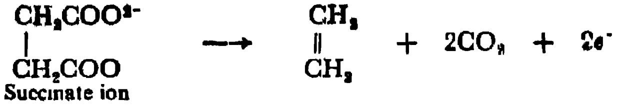

ETHANOL (1 VOL.) + H_2SO_4 (1 VOL.)
ETHANOL (1 VOL.)+ H_2SO_4 (2½ VOL.)
ETHYLENE
NaOH

Fig. 14·3—Preparation of ethylene in the laboratory.

(*ii*) ***Electrolysis of an aqueous solution of sodium or potassium salt of succinic acid*** (**Kolbe's reaction**) also produces ethylene (*cf.* Kolbe's reaction for the preparation of paraffins, *e.g.*, ethane by electrolysis of sodium acetate solution).

At anode :

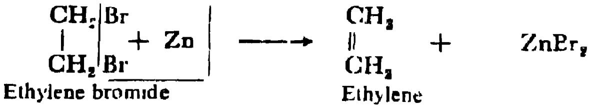


$$\underset{\text{Succinate ion}}{\begin{matrix}CH_2COO^{-}\\ |\\ CH_2COO\end{matrix}} \longrightarrow \begin{matrix}CH_2\\ \|\\ CH_2\end{matrix} + 2CO_2 + 2e^-$$

At cathode :

$$2H_2O + 2e^- \longrightarrow 2OH^- + H_2\uparrow$$

(*iii*) A pure sample of ethylene can be prepared by *warming granulated zinc with an alcoholic solution of ethylene bromide* or by dropping ethylene bromide into zinc-dust suspended in alcohol and glacial acetic acid.



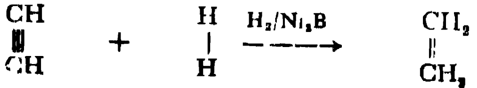
$$\underset{\text{Ethylene bromide}}{\begin{matrix}CH_2\,|\,Br\\ |\quad + Zn\\ CH_2\,|\,Br\end{matrix}} \longrightarrow \underset{\text{Ethylene}}{\begin{matrix}CH_2\\ \|\\ CH_2\end{matrix}} + ZnBr_2$$

Manufacture. Ethylene is prepared industrially by the following methods :

(*i*) *By passing ethanol vapours over heated alumina at about 620K.*

$$C_2H_5OH \longrightarrow C_2H_4 + H_2O$$

(*ii*) *By the partial hydrogenation of acetylene.* Acetylene is mixed with hydrogen and passed over a catalyst at 470K. Different catalysts which may be used are P-2 catalyst (nickel boride, Ni_2B) or Lindlar's catalyst (Metallic palladium deposited on $CaCO_3$ or $BaSO_4$ partially poisoned with quinoline).



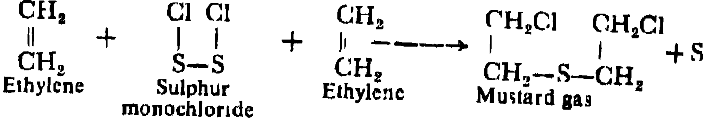
$$\begin{matrix}CH\\ |||\\ CH\end{matrix} + \begin{matrix}H\\ |\\ H\end{matrix} \xrightarrow{H_2/Ni_2B} \begin{matrix}CH_2\\ \|\\ CH_2\end{matrix}$$

(*iii*) Large quantities of ethylene are being obtained as a by-product in the cracking of petroleum.

Properties of Ethylene : Physical. Ethylene is a colourless gas with faint sweet smell. It is sparingly soluble (almost insoluble) in water but readily soluble in organic solvents such as ether and alcohol. If inhaled in a large quantity, it produces unconsciousness.

Chemical. Important reactions of ethylene have already been discussed under General Reactions of Olefins.

Uses of Ethylene. (*i*) In World War I (1914-18) it was used for the manufacture of mustard gas.



$$\underset{\text{Ethylene}}{\begin{matrix}CH_2\\ \|\\ CH_2\end{matrix}} + \underset{\text{Sulphur monochloride}}{\begin{matrix}Cl\quad Cl\\ |\quad\ |\\ S{-}S\end{matrix}} + \underset{\text{Ethylene}}{\begin{matrix}CH_2\\ \|\\ CH_2\end{matrix}} \longrightarrow \underset{\text{Mustard gas}}{\begin{matrix}CH_2Cl\qquad CH_2Cl\\ |\qquad\qquad |\\ CH_2{-}S{-}CH_2\end{matrix}} + S$$

(*ii*) It is also used as an anaesthetic.

(*iii*) Due to the ease with which it can be transported in cylinders under high pressure, it is used in place of acetylene for welding purposes.

(*iv*) Its main use is in the fruit industry for the preservation and artificial ripening of green fruits like oranges, bananas and apples.

(*v*) In the manufacture of plastics and various solvents such as glycol, dioxan, etc.

Tests. (*i*) Ethylene decolorises bromine water and alkaline potassium permanganate solution (Baeyer's reagent).

(*ii*) It is absorbed by concentrated sulphuric acid.

(*iii*) With ammoniacal silver nitrate there is no action—Distinction from acetylene.

8. Orbital Hybridization and the Structure of Alkenes. Let us consider the simplest alkene, ethene. In this the carbon atoms are in a state of sp^3 hybridization. The molecule is coplanar, *i.e.*, all its nuclei lie in the same plane (Fig. 14·4). The H—C—C bond angles of ethene are known to be ~121° and H—C—H bond angles are ~118° which are quite close to the value 120° that we would expect on the basis of sp^2-hybridized carbon atoms.

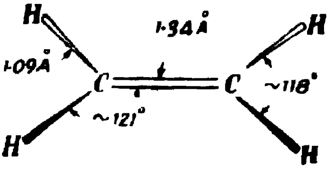


Fig 14·4—Coplanar molecule of ethylene and its bond angles and bond distances.

There are five sigma bonds (4C—H bonds and one C—C bond) and one pi bond (C=C double bond is a combination of one sigma and one pi bond). Their formation has been explained on page 1·73. C=C bond distance in ethylene is 1·34Å (*cf.* bond distance = 1·54Å in C_2H_6) and C—H bond distance is 1·09Å in comparison to 1·10Å in ethane.

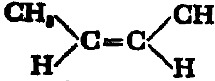
As stated above C—H bonds in ethene are slightly shorter than those in ethane. We can explain the difference in the two bond lengths as follows :

Since an *s* orbital is smaller than a *p* orbital, the bond length of a molecular orbital decreases as the amount of *s* character in a hybrid orbital increases. In sp^3 hybrid orbital the amount of *s* character is 25% and in sp^2 hybrid orbital it is 33%. Hence sp^2 hybrid orbitals of ethene have more *s* character than the sp^3 hybrid orbitals of ethane. On this account the sp^2 orbitals are shorter than the sp^3 orbitals Hence C—C bond in ethylene formed by sp^2-sp^2 overlap is shorter than the C—C bond in ethane formed by sp^3-sp^3 overlap. Similarly, C—H bonds formed by sp^2 hybrid orbitals (by sp^2 *s* overlap) are shorter than those formed by sp^3 hybrid orbitals (by sp^3-*s* overlap).

9. Heats of Hydrogenation and Stability of Alkenes.—Hydrogenation of alkenes is an exothermic reaction and heat of reaction is ~125·5 kJ mol^{-1}. Heats of hydrogenation of individual alkenes differ from this average value by more than

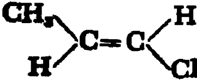
3kJ mol^{-1}. These values are often used to determine their relative stabilities. For example consider the heats of hydrogenation of three butene isomers.

$$\underset{\text{1-Butene}}{CH_3CH_2CH{=}CH_2} + H_2 \rightarrow \underset{\text{Butane}}{CH_3CH_2CH_2CH_3}\ ;\ \Delta H = -126{\cdot}8\ kJ\ mol^{-1}$$



cis-2-Butene

$$+H_2 \rightarrow \underset{\text{Butane}}{CH_3CH_2CH_2CH_3}\ ;\ \Delta H = -119{\cdot}7\ kJ\ mol^{-1}$$



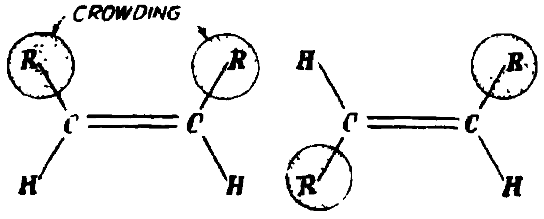
trans-2-Butene

$$+H_2 \rightarrow \underset{\text{Butane}}{CH_3CH_2CH_2CH_3}\ ;\ \Delta H = -115{\cdot}5\ kJ\ mol^{-1}$$

Product of reaction (butane) and one of the reactants (hydrogen) are the same in each case. Their different heats of reaction must, therefore, be related to different heat contents (or different relative stabilities) of the three individual butenes.

1-Butene which evolves the largest amount of heat, must have the greatest potential energy and should, therefore, be the least stable isomer. On similar reasoning, the *trans*-isomer which evolves the least heat, must have the lowest potential energy and be the most stable isomer. The potential energy (and hence stability) of *cis*-isomer falls in between the other two isomers.

In a *cis*-isomer the two alkyl groups lie on the same side of the double bond. The crowding of the two alkyl groups causes strain and results in greater potential energy of the *cis*-isomer, in comparison to that of *trans*-isomer.



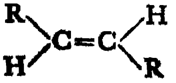
cis-isomer *trans*-isomer

Fig. 14·5—The less stable *cis*-isomer has greater strain due to crowding of alkyl groups.

As a result of studies of large number of alkenes, we have discovered the following pattern of stabilities which is related to the number of alkyl groups attached to the carbon atoms of the double bond.

The greater the number of alkyl groups attached to the doubly bonded carbon atoms (*i.e., the more highly substituted is the double bond*) *the more stable the alkene.* We can represent this order of stabilities in general terms as follows :

$R_2C{=}CR_2$ > $R_2C{=}CHR$ >



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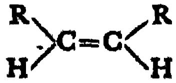
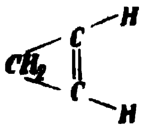
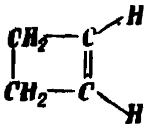


$\approx R_2C{=}CH_2$ > $RCH{=}CH_2$ > $CH_2{=}CH_2$

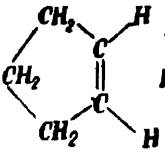
10. Cycloalkenes.—Cyclic hydrocarbons having one double bond are termed cycloalkenes. Lower members cyclopropene to cyclohexene exist only in *cis* form. Higher ones can exist in both *cis* and *trans*-forms.



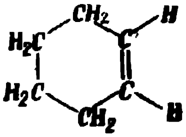
cis-cyclopropene



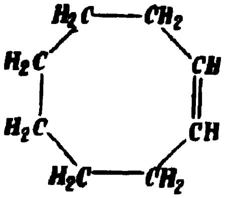
cis-cyclobutene



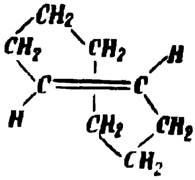
cis-cyclopentene



cis-cyclohexene



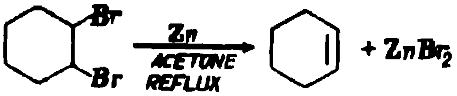
cis-cyclooctene



trans-cyclooctene

These can be prepared by methods used for the preparation of alkenes and also resemble them in properties. For example, cycloalkenes are prepared :

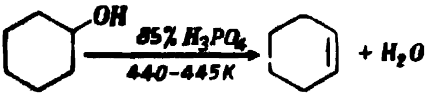
(*i*) *By dehalogenation.*



1,2-dibromo-cyclohexane (*cis* or *trans*)

Cyclohexene

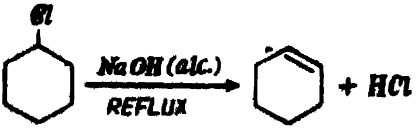
(*ii*) *By dehydration of cycloalkanols.*



Cyclohexanol

Cyclohexene

(*iii*) *By dehydrohalogenation of cycloalkyl halides.*

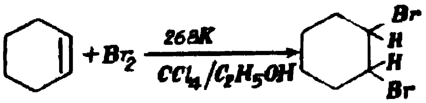


Chloro-cyclohexane

A few reactions of cycloalkenes are :

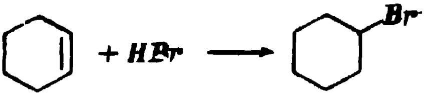
(a) ***Addition reactions* :**

(i)



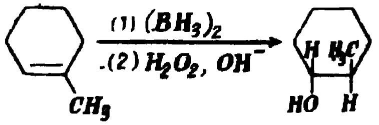
trans-1,2-Dibromo-cyclohexane

(ii)



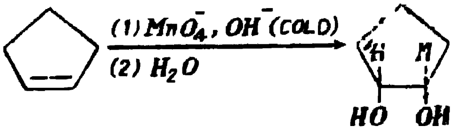
Cyclohexyl bromide

(iii)



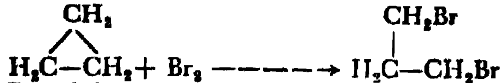
1-Methylcyclohexene *trans*-2-Methyl-cyclohexanol

(b) ***Oxidation with*** $KMnO_4$ *(alkaline) or* OsO_4.



Cyclopentene *cis*-1,2-cyclopentanediol

11. Baeyer's Strain Theory.—Olefins are very reactive and the double bond in them is very unstable. The double bond readily opens and gives addition product. Similarly, cycloparaffins are sufficiently unstable. For example, trimethylene ring opens like a double bond and gives addition products.



Trimethylene Trimethylene dibromide

The instability of the double bond or cycloparaffin ring and reactivity of unsaturated compounds containing one or more double bond has been explained by a German chemist Adolf von Baeyer* in a theory known after his name as **Baeyer's strain theory.**

---

* **Adolf von Baeyer** (1835-1917)—German organic chemist who evolved a strain theory of carbon rings in 1885, to account for the instability of unsaturated compounds. He was awarded the Nobel Prize for Chemistry in 1905.

Le Bel and van't Hoff postulated in 1874 that the carbon atom lies at the centre of a regular tetrahedron towards the four corners of which its four valency bonds are directed (*see* page 1·71). The angle between any two valency bonds is 109° 28′.

According to Baeyer's strain theory, put forward in 1885, *the valency angle can be altered from this normal value (109° 28′) by bending of the valency bonds. But due to this bending of valency bonds a strain is set up in the molecule. Greater the deviation from the normal angle, the greater is the strain and greater the instability of the organic compound.*

This affords an easy explanation for the following :

(*a*) Stability of saturated compounds ;

(*b*) Relative stability of ring compounds ;

(*c*) Instability of unsaturated compounds ; and

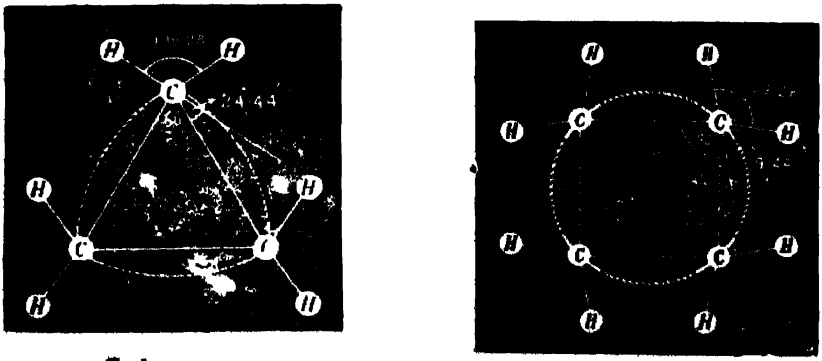
(*d*) Mechanism of addition reactions.

(*a*) **Stability of Saturated Compounds.** In saturated compounds various carbon atoms present are linked through single bonds. There is a free rotation round the single bond and the groups attached to the carbon atom are capable of free disposition in space.

Under these conditions there is no bending of valency bonds and hence no deviation from the normal angle (129° 28′). There is thus no strain in the molecule and in the absence of any strain the saturated compounds are very stable.

(*b*) **Relative Stability of Ring Compounds.** In the case of trimethylene or cyclopropane the carbon atoms lie at the three corners of an equilateral triangle. The angle between their valency bonds engaged in C—C linkages is 60°, *i.e.*, there is a deviation of (109° 28′−60°)=49° 28′ from the normal angle (109° 28′). In other words, each valency bond has been deviated through half this angle (=24° 44′).

In cyclobutane the four carbon atoms are situated at the four corners of a square. The angle between the valency bonds engaged



Cyclopropane Cyclobutane

Fig. 14·6—Atomic models of cyclopropane and cyclobutane.

in C—C linkages is 90°, *i.e.*, there is a deviation of (109° 28′—90°) =19° 28′ from the normal angle (109° 28′). In other words, each valency bond has been deviated through half this angle (=9° 44′).

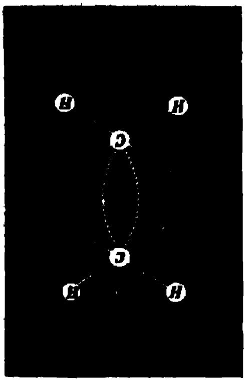


Fig. 14·7—Atomic model of a double bond.

Double bond is a limiting case of a ring system with zero angle between its valency bonds. Here each valency bond has suffered a deviation

=(109° 28′—0)=54° 44′.

The deviations or bendings of valency bonds from the normal angle (109° 28′) in various cycloparaffins can be calculated in a similar manner and are given below :

Ring	*Deviation*	*Ring*	*Deviation*
Double bond	+54° 44′	Cyclopentane	+0° 44′
Cyclopropane	+24° 44′	Cyclohexane	—5° 16′
Cyclobutane	+9° 44′	Cycloheptane	—9° 33′

(+) sign indicates the bending of valency bonds inwards whereas (—) sign indicates bending of valency bonds outwards.

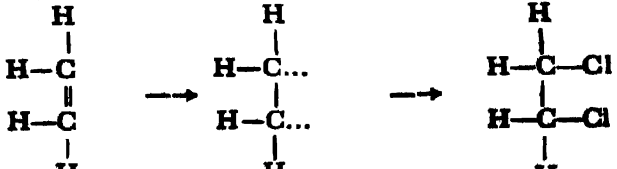
According to the Strain Theory, the strain is directly proportional to the deviation from the normal angle. Thus the above figures indicate that the strain is minimum in cyclopentane and maximum in cyclopropane. In the case of double bond strain is greater than even cyclopropane.

Further instability being directly proportional to strain, cyclopentane is more stable than cyclobutane or cyclopropane and double bond is the least stable of all. These deductions are fully borne out by their chemical reactions.

(*c*) **Instability of Unsaturated Compounds.** Unsaturated compounds contain double or triple bonds which involve bending of valency bonds. Due to bending of valency bonds from the normal angle there is strain in the molecule. Instability of unsaturated compounds is due to this strain.

(*d*) **Mechanism of Addition Reactions.** Addition reactions are characteristic of various unsaturated compounds containing a double or a triple bond.

In an addition reaction, *e.g.*, chlorination of ethylene, the double bond breaks up due to strain in the molecule and two valencies are set free. Two chlorine atoms are taken up, one at each valency set free.



$$\begin{array}{c}\text{H}\\|\\\text{H—C}\\\|\\\text{H—C}\\|\\\text{H}\end{array}\longrightarrow\begin{array}{c}\text{H}\\|\\\text{H—C...}\\|\\\text{H—C...}\\|\\\text{H}\end{array}\longrightarrow\begin{array}{c}\text{H}\\|\\\text{H—C—Cl}\\|\\\text{H—C—Cl}\\|\\\text{H}\end{array}$$

Ethylene with a double bond

Ethylene with double bond ruptured and two valencies set free in presence of chlorine.

Addition product—Ethylene chloride.

12. Theory of Strainless Rings.—According to Baeyer, the carbon atoms of a ring lie in the same plane. The strain was calculated on the assumption of planar rings. The strain is minimum for cyclopentane and goes on increasing as the size of the ring increases. Hence members higher than cyclopentane should be increasingly unstable.

A parallel exists between the ease of formation of a ring and its stability. This implies that very large rings should be difficult, if at all possible, to prepare due to the great strain involved in the ring. Chemical stability of a ring can be measured from its heat of combustion per methylene group as given in Table 14·1.

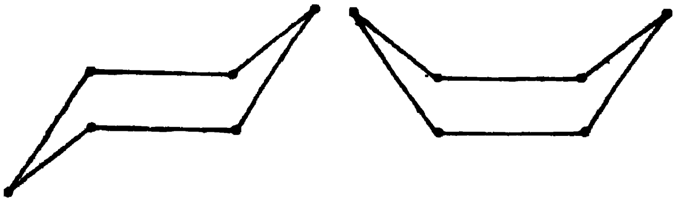
According to results shown in Table 14·1, heat of combustion per methylene group decreases or, in other words, the stability increases up to five- and six-membered rings and then remains constant.

Table 14·1—Heats of Combustion

Number of carbon atoms in the rings	Heat of combustion in kJ per methylene group	Deviation from the normal angle
2 (*Ethylene*)	711	+54° 44′
3 (*Cyclopropane*)	697	+24° 44′
4 (*Cyclobutane*)	685	+ 9° 44′
5 (*Cyclopentane*)	664	+ 0° 44′
6 (*Cyclohexane*)	659	− 5° 16′
7 (*Cycloheptane*)	662	− 9° 33′
8 *and higher*	661-665	−12° 46′ and higher

Thus contradictory results are obtained from the internal strain data and chemical stability from heat of combustion data. The apparent anomaly was explained by Sachse in 1890 by rejecting the postulate that all rings are planar and by assuming that *rings with six or more carbon atoms are puckered. These are strainless as the carbon atoms lie in different planes and the normal valency angle is retained.*

According to Sachse cyclohexane exists in two forms 'boat' or C form and 'chair' or Z form as given below (Fig. 14·8). The two



'Chair' or Z form. 'Boat' or C form.

Fig. 14·8—Strainless cyclohexane rings.

forms have not been isolated so far. This is explained by saying that the energy of interconversion of the two forms being very small (20·9 kJ per mole) one form readily changes into the other.

Mohr (1918) further elaborated this theory and applied it to compounds with the two rings fused together.

Ruzicka* and others have succeeded in preparing ring compounds up to thirty-four carbon atoms in the ring and these have been found to be remarkably stable. Their stability could only be explained on the assumption of strainless rings.

13. Coulson and Moffit's Concept of Maximum Overlapping of Carbon Orbitals.—In the light of valency bond theory the reactivity of double bond is explained by the π electrons. When four identical groups are attached to a carbon atom, the four carbon valencies are equivalent and the valency angle is 109° 28′. When the four groups are different, the four valencies are not equivalent and these now point towards the four corners of an *irregular tetrahedron.*

According to Baeyer's strain theory, the configuration of cyclopropane is an equilateral triangle with valency angles of 60°. This value is impossible as the carbon valency angles can never be less than 90° (when these are pure p-orbitals). The angles are more than 90° when hybridisation occurs.

According to Coulson, the smallest carbon valency angle which one can reasonably expect to have is 104°. He, therefore, suggested that in cyclopropane only a partial overlap of the sp^3-hybrid† orbittals occurs, so that *the C—C—C bond angle is decreased slightly (104°) and the H—C—H angle (120°) is opened* from the normal tetrahedral angle. *In fact the carbon orbitals overlap at an angle to give so-called bent bonds* (*see* Fig. 14·9). This decrease in overlap results in weakening of the bonds and explains the instability of cylopropane.

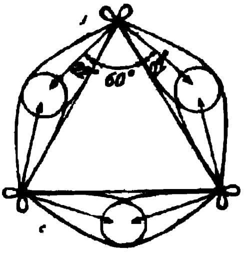


Fig. 14·9—Incomplete orbital overlap in cyclopropane.

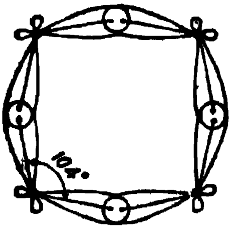


Fig. 14·10—Incomplete orbital overlap in cyclobutane.

Applying the same argument to cyclobutane (Fig. 14·10), we see that this molecule also has bent bonds but the decrease in overlap is less than in the case of cyclopropane. Cyclobutane is, therefore, more stable and less reactive than cyclopropane.

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* **Ruzicka, Leopold W. G.** (1887—)—Swiss chemist, he was the first to synthesise musk. He did distinguished work on polymethylenes, higher terpenes and on organic synthesis. He shared the Nobel Prize for Chemistry with Butenandt and in 1939 for their synthesis of sex hormones.

† It is not pure sp^3- hybridisation as in saturated aliphatic C—C bonds.

Modern theory thus offers the concept of incomplete orbital overlap as a measure of the classical Baeyer strain.

DIOLEFINS OR ALKADIENES

14. Nomenclature.—Compounds containing two double bonds are called diolefins or alkadienes and have the general formula C_nH_{2n-2} (same as that of alkynes).

To name a diolefin select the longest chain containing the two double bonds as the parent alkane and indicate the positions of side-chains and double bonds by numbers. For example,

$CH_2{=}CH{-}CH{=}CH_2$ is, 1, 3-butadiene and

$$\overset{\displaystyle CH_3}{\overset{|}{CH_2{=}C}}{-}CH{=}CH_2$$ is 2-methyl-1, 3-butadiene or **Isoprene.**

An alkadiene may have :

(*i*) *isolated double bonds* as in diallyl or 1, 5-hexadiene,

$$CH_2{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2$$

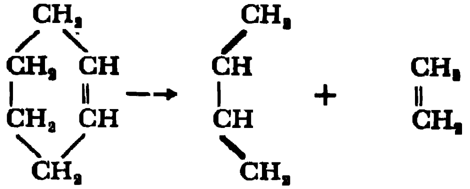
(*ii*) *cumulated double bonds* as in allene or propadiene.

$$CH_2{=}C{=}CH_2\cdot$$

(*iii*) *conjugated double bonds* as in 1, 3-butadiene.

15. Preparation and Properties.—Alkadienes can be prepared by methods similar to those employed for the preparation of olefins. For example,

Butadiene may be prepared by passing cyclohexene over a heated nichrome wire.



(65·75%)

It is, however, prepared technically :

(*i*) *By dehydrogenation of alkanes or alkenes by passing the vapour over heated catalyst* (Cr_2O_3 on an alumina support at 800-900 K).

$$\underset{n\text{-butane}}{CH_3.CH_2.CH_2.CH_3} \xrightarrow[-2H_2]{Cr_2O_3} \underset{1,3\text{-butadiene}}{CH_2{=}CH{-}CH{=}CH_2}$$

$$\underset{1\text{-Butene}}{CH_2{=}CH.CH_2.CH_3} \xrightarrow[-H_2]{Cr_2O_3} \underset{1,3\text{-Butadiene}}{CH_2{=}CH{-}CH{=}CH_2}$$

(*ii*) *By passing a mixture of 1, 3-butanediol and steam in the ratio 4 : 1, over trisodium phosphate+H_3PO_4 (20%) at 540K.*

$$CH_3CHOH.CH_2.CH_2OH \xrightarrow{-2H_2O} CH_2{=}CH{-}CH{=}CH_2 \quad (85\text{-}90\%)$$

(*iii*) *By passing a mixture of ethanol and acetaldehyde vapours over heated catalyst* (silica gel+2% tantalum oxide).

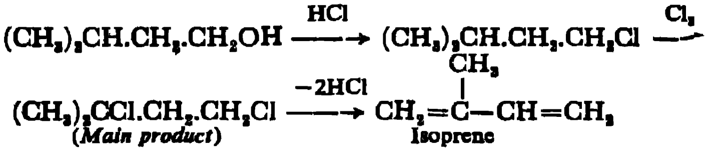
$$C_2H_5OH + CH_3CHO \longrightarrow CH_2=CH-CH=CH_2 + 2H_2O$$

(*iv*) *By passing a mixture of acetylene and formaldehyde over copper acetylide (catalyst) followed by catalytic hydrogenation of the intermediate product butynediol.*

$$CH\equiv CH + 2HCHO \xrightarrow{Cu_2C_2} CH_2OH.C\equiv C.CH_2OH \xrightarrow{H_2/Ni}$$

$$CH_2OH.CH_2.CH_2.CH_2OH \xrightarrow{-2H_2O} CH_2=CH-CH=CH_2$$

Similarly, isoprene is prepared by heating isopentyl alcohol with hydrogen chloride, chlorinating the isoamyl chloride and passing the resulting dichloride over soda-lime heated at 770K.

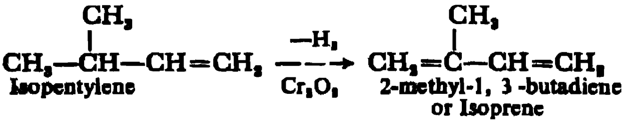


$$(CH_3)_2CH.CH_2.CH_2OH \xrightarrow{HCl} (CH_3)_2CH.CH_2.CH_2Cl \xrightarrow{Cl_2}$$

$$\underset{(Main\ product)}{(CH_3)_2CCl.CH_2.CH_2Cl} \xrightarrow{-2HCl} \underset{Isoprene}{CH_2=\overset{\overset{CH_3}{|}}{C}-CH=CH_2}$$

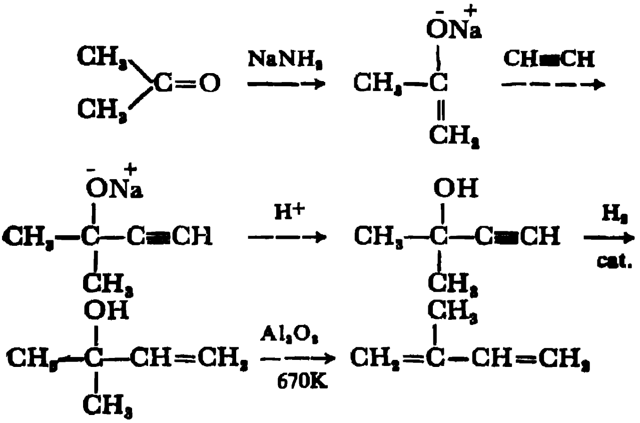
It is prepared industrially :

(*i*) *By passing isopentane or isopentylene over heated Cr_2O_3 on an alumina support.*



$$\underset{Isopentylene}{CH_3-\overset{\overset{CH_3}{|}}{C}H-CH=CH_2} \xrightarrow[Cr_2O_3]{-H_2} \underset{\text{2-methyl-1, 3-butadiene or Isoprene}}{CH_2=\overset{\overset{CH_3}{|}}{C}-CH=CH_2}$$

(*ii*) *From acetone as given below* :



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=O \xrightarrow{NaNH_2} CH_3-\overset{\overset{\overset{-\ \ +}{ONa}}{|}}{\underset{\underset{CH_2}{\|}}{C}} \xrightarrow{CH\equiv CH}$$

$$CH_3-\overset{\overset{\overset{-\ \ +}{ONa}}{|}}{\underset{\underset{CH_3}{|}}{C}}-C\equiv CH \xrightarrow{H^+} CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-C\equiv CH \xrightarrow[cat.]{H_2}$$

$$CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH=CH_2 \xrightarrow[670K]{Al_2O_3} CH_2=\overset{\overset{CH_3}{|}}{C}-CH=CH_2$$

Butadiene is a gas (b.p. 271·6K). In the presence of metallic sodium (catalyst) butadiene polymerises to give a rubber substitute called *buna* (*butadiene*+*Na*).

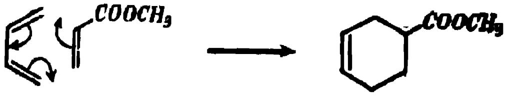
Isoprene is a liquid (b.p. 308K). On heating with metallic sodium at 339K it polymerises to give a product resembling natural rubber.

These give usual reactions of hydrocarbons containing two double bonds. Properties of alkadienes containing alternate double and single bonds (conjugated systems) are abnormal. For example, these undergo abnormal addition reactions and readily polymerise.

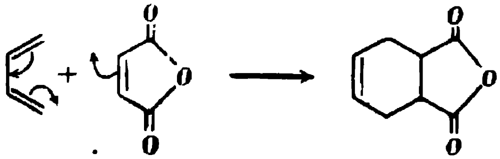
The abnormal behaviour of conjugated alkadienes is due to delocalisation of electrons as explained on page 1·101.

Some other typical reactions of conjugated dienes are :

(*i*) **Diels-Alder Addition.** It is an exceedingly useful reaction used for synthesising cyclic systems. A conjugated diene is treated with an alkene (usually substituted with an electron-withdrawing group) called a *dienophile*. For example,



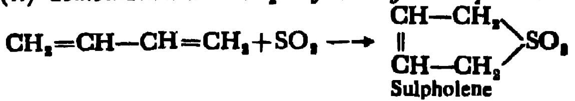
butadiene dienophile adduct



butadiene maleic anhydride (dienophile) adduct

The mechanism suggested above is a one-step process. This is supported by the fact that reaction is not sensitive to polarity of the solvent suggesting thereby the absence of charged transition states or charged intermediates.

(*ii*) *Combination with SO_2 to give a cyclic sulphone.*



$$CH_2{=}CH{-}CH{=}CH_2 + SO_2 \longrightarrow \begin{array}{l} CH{-}CH_2 \\ \| \qquad\quad \rangle SO_2 \\ CH{-}CH_2 \end{array}$$

Sulpholene
(*a cyclic sulphone*)

16. **Thiele Theory of Partial Valencies.**—Alkadienes with conjugated system of double bonds undergo abnormal addition reactionns, *e.g.*, when 1, 3-butadiene is treated with bromine (one molecule), two dibromo derivatives are obtained. One of these is expected 3, 4-dibromo 1-butene (1 : 2 addition) and the other is unexpected 1, 4-dibromo 2-butene (1 : 4 addition).

$$\underset{\text{1, 3-Butadiene}}{CH_2{=}CH{-}CH{=}CH_2} \xrightarrow{Br_2} \underset{\text{3, 4-dibromo 1-butene}}{CH_2Br{-}CHBr{-}CH{=}CH_2}$$
$$+\underset{\text{1, 4-dibromo-2-butene}}{CH_2Br{-}CH{=}CH{-}CH_2Br}$$

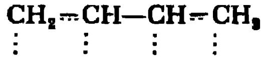
It has been found that both of these products are obtained together and their relative amounts depend on—

(*i*) Nature of the substance being added.

(*ii*) Nature of the solvent.

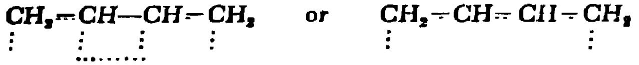
(*iii*) Other conditions, temperature, etc.

Thiele suggested in 1899 his *theory of partial valencies* to account for the unexpected 1, 4-addition. According to him a single bond is enough to hold two carbon atoms together. In the case of a double bond the two valencies are not fully used in linking the two carbon atoms together. Out of the two valencies only one and a part of the other is actually used up. A part of the second valency is left as surplus on each carbon atom. Thiele called this surplus valency the *residual* or *partial* valency. Representing the partial valencies by dotted lines the formula of butadiene can be written as:



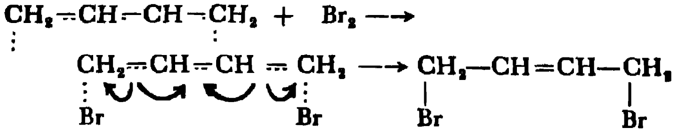
$$CH_2=CH-CH=CH_2$$

Thiele postulated that the partial valencies on middle carbon atoms satisfy each other mutually. Thus the actual state of affairs *can be presented as*



$$CH_2=CH-CH=CH_2 \quad \text{or} \quad CH_2=CH=CH=CH_2$$

Addition of bromine, etc., occurs at the ends first by attachment through the partial valencies and then by each bromine atom acquiring a full valency. As a result of it the two middle carbon atoms utilise completely the two valencies left and a double bond results between them.

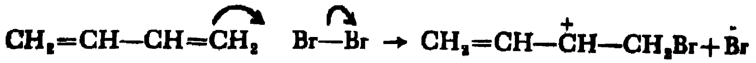


$$CH_2=CH=CH=CH_2 + Br_2 \longrightarrow CH_2=CH=CH=CH_2 \longrightarrow CH_2-CH=CH-CH_2$$

Thiele's theory explains 1, 4-addition very nicely but fails to explain 1, 2-addition.

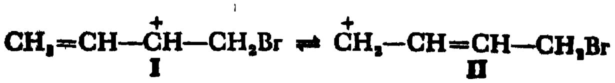
In terms of the modern theory the 1,2 and 1,4 addition can be explained as follows :

(*i*) In the vicinity of a π electron cloud bromine molecule has a tendency to separate into positive and negative ions ($\overset{\delta+}{Br}-\overset{\delta}{Br}$). This approaches the butadiene molecule forming a transition complex which breaks down as follows :



$$CH_2=CH-CH=CH_2 \quad Br-Br \rightarrow CH_2=CH-\overset{+}{C}H-CH_2Br+\overset{-}{Br}$$

(*ii*) The resulting carbocation ion is capable of forming a resonance hybrid as follows :

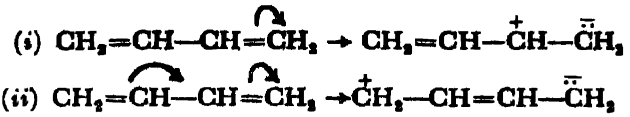


$$\underset{\text{I}}{CH_2=CH-\overset{+}{C}H-CH_2Br} \rightleftharpoons \underset{\text{II}}{\overset{+}{C}H_2-CH=CH-CH_2Br}$$

(*iii*) Addition of the negative bromide ion Br^- to this carbocation can occur at either positive carbon resulting in 1, 2 and 1, 4-addition.

It has been found that in a non-ionizing medium (*e.g.*, hexane) 1, 2-addition is more (about 62%) while in an ionizing solvent (*e.g.*, acetic acid), it is mainly 1, 4-addition (about 70%). This is explained as follows :

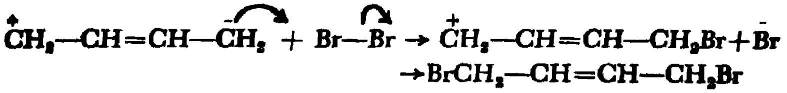
(*a*) **1, 4-addition.** Butadiene can undergo the electromeric effect in two stages given below :



(*i*) $CH_2{=}CH{-}CH{=}CH_2 \rightarrow CH_2{=}CH{-}\overset{+}{C}H{-}\overset{-}{\ddot{C}}H_2$

(*ii*) $CH_2{=}CH{-}CH{=}CH_2 \rightarrow \overset{+}{C}H_2{-}CH{=}CH{-}\overset{-}{\ddot{C}}H_2$

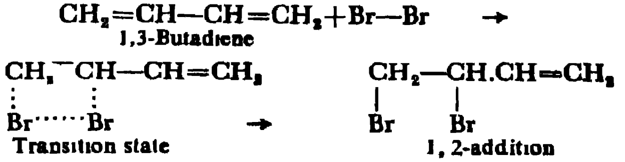
The second product is more stable because in this the charges are farther apart as compared with the first. In an ionizing solvent the addition of bromine takes place as follows :



$$\overset{+}{C}H_2{-}CH{=}CH{-}\overset{-}{C}H_2 + Br{-}Br \rightarrow \overset{+}{C}H_2{-}CH{=}CH{-}CH_2Br + \overset{-}{Br}$$
$$\rightarrow BrCH_2{-}CH{=}CH{-}CH_2Br$$

During addition in an ionizing medium the bromine atom breaks off readily as Br^- ion which then attacks the terminal carbon atom carrying + charge resulting in 1, 4-addition.

(*b*) **1,2-Addition.** In a non-ionizing solvent it may be that bromine molecule tends to add on as a whole to one of the double bonds by a broadside attack.



$$\underset{\text{1,3-Butadiene}}{CH_2{=}CH{-}CH{=}CH_2} + Br{-}Br \rightarrow$$

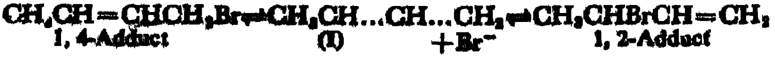
$$\underset{\text{Transition state}}{\begin{array}{l} CH_2{-}CH{-}CH{=}CH_2 \\ \vdots \quad\;\; \vdots \\ Br \cdots\cdots Br \end{array}} \rightarrow \underset{\text{1, 2-addition}}{\begin{array}{l} CH_2{-}CH.CH{=}CH_2 \\ | \qquad\; | \\ Br \quad\; Br \end{array}}$$

Effect of Temperature. It has been found that during addition of HBr to 1,3-butadiene, the 1,2-addition product ($CH_2{=}CH{-}CHBr{-}CH_3$) is formed in larger proportion at lower temperature whereas 1, 4-addition product ($CH_3CH{=}CH{-}CH_2Br$) predominates at higher temperature. For example at 350K yield of 1, 2-adduct is 80% in comparison to 20% at 310 K. The effect of temperature can be explained as follows :

The proportion of the two products obtained at low temperatures is determined by the **rate** of addition where as that obtained at higher temperature is determined by the equilibrium between the two isomers.

(*i*) E_{act} for the reaction leading to 1, 2-addition is less than that for 1, 4-addition. As such rate of 1, 2-addition is higher than that of 1, 4-addition. At lower temperature the 1, 2-Adduct which is formed faster, is in excess

(*ii*) The two addition products on ionization form the same carbocation (I).



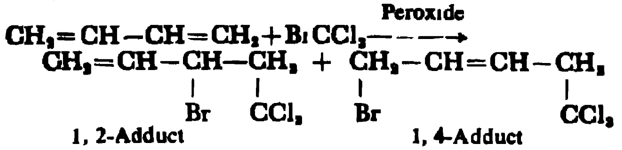
$$\underset{\text{1, 4-Adduct}}{CH_3CH{=}CHCH_2Br} \rightleftharpoons \underset{\text{(I)}}{CH_3\overset{\delta+}{C}H \ldots CH \ldots \overset{\delta+}{C}H_2} + Br^- \rightleftharpoons \underset{\text{1, 2-Adduct}}{CH_3CHBrCH{=}CH_2}$$

1, 4-Adduct is more stable than the 1,2-Adduct. Energy difference between 1,2-adduct and the carbocation (I) is, therefore, less than that between 1,4-adduct and the carbocation. Ionization of 1,2-adduct is, therefore, easier than that of 1, 4-adduct.

At lower temperature ionization o both adducts is very small and 1,2-adduct which is formed at a rapid rate is present in large proportion.

At higher temperature ionization becomes important. 1,2-*adduct ionizes more readily in comparison to 1, 4-adduct. As such the 1, 4-adduct though formed slowly accumulates since it does not ionise readily.* At the equilibrium point, 1, 4-adduct is, therefore, the major product.

17. Free Radical Addition Reactions of Conjugated Dienes.—Under certain conditions addition to a conjugated diene may be a free radical addition reaction. However, in this case also it leads to the formation of both 1,2- and 1,4-addition products. For example, addition of $BrCCl_3$ to 1, 3-butadiene in presence of a peroxide is a free radical addition leading to both 1, 2- and 1, 4-adducts.



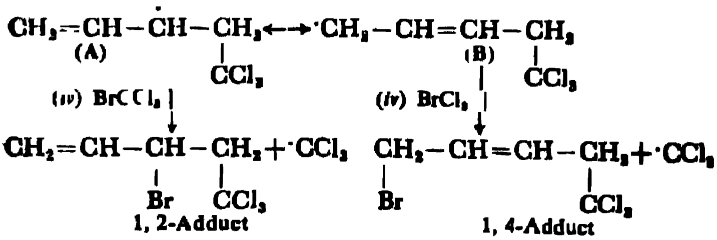
$$CH_2=CH-CH=CH_2+BrCCl_3 \xrightarrow{\text{Peroxide}} \underset{\text{1, 2-Adduct}}{CH_2=CH-\underset{Br}{\underset{|}{CH}}-\underset{CCl_3}{\underset{|}{CH_2}}} + \underset{\text{1, 4-Adduct}}{\underset{Br}{\underset{|}{CH_2}}-CH=CH-\underset{CCl_3}{\underset{|}{CH_2}}}$$

Mechanism of the Reaction :

(*i*) Peroxide→Rad·

(*ii*) Rad· + $BrCCl_3$→Rad—Br + ·CCl_3 Free radical

(*iii*) $CH_2=CH-CH=CH_2$ + CCl_3 ⟶



$$\underset{(A)}{CH_2=CH-\dot{C}H-\underset{CCl_3}{\underset{|}{CH_2}}} \longleftrightarrow \underset{(B)}{\cdot CH_2-CH=CH-\underset{CCl_3}{\underset{|}{CH_2}}}$$

$$\downarrow (iv)\ BrCCl_3 \qquad\qquad \downarrow (iv)\ BrCl_3$$

$$\underset{\text{1, 2-Adduct}}{CH_2=CH-\underset{Br}{\underset{|}{CH}}-\underset{CCl_3}{\underset{|}{CH_2}}+\cdot CCl_3} \qquad \underset{\text{1, 4-Adduct}}{\underset{Br}{\underset{|}{CH_2}}-CH=CH-\underset{CCl_3}{\underset{|}{CH_2}}+\cdot CCl_3}$$

(*i*) and (*ii*) are the chain-initiating steps whereas (*iii*) and (*iv*) are the chain-propagating steps.

The product of step (*iii*) is a resonance hybrid of two structures (A) and (B) which in step (*iv*) react with $BrCCl_3$ to yield 1, 2 and 1, 4-adducts respectively.

Conjugated dienes are more stable than simple alkenes but the free radical addition to conjugated dienes is faster than addition to simple alkenes.

How can we explain this unexpected reactivity of conjugated dienes towards free radical addition ? This is due to much greater stability of the intermediate free radical obtained (stabilised by resonance) compared to the stability of intermediate free radical obtained from simple alkenes. Ease for the formation of the former free radical is, therefore, much less than that for the formation of the latter free radical. Because of this the free radical addition to dienes proceeds at a faster rate.

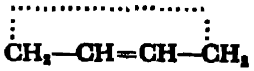
18. Relative Stabilities of Dienes.—Conjugated dienes have been found to be more stable than the other dienes. For example, heat of hydrogenation of 1, 4-pentadiene is 254·4 kJ mol^{-1} and that of *1, 3-pentadiene is only 234·3 kJ mol^{-1} showing thereby the latter (a conjugated diene) is more stable than the former.* Greater stability of the conjugated dienes is explained as follows :

(*i*) **Due to Resonance.** A conjugated diene forms a resonance hybrid of the following structures :

$$\underset{\text{(I)}}{CH_2{=}CH{-}CH{=}CH_2} \longleftrightarrow \underset{\text{(II)}}{CH_2{=}CH{-}\overset{+}{C}H{-}\overset{-}{C}H_2} \longleftrightarrow \underset{\text{(III)}}{\overset{+}{C}H_2{-}CH{=}CH{-}\overset{-}{C}H_2}$$

However, there is still another contributing structure given below :

$$\underset{\substack{\text{A diradical}\\ \text{(IV)}}}{\dot{C}H_2{-}CH{=}CH{-}\dot{C}H_2}$$



$CH_2{-}CH{=}CH{-}CH_2$

(V)

There are two electrons with antiparallel spin in (IV), since the number of unpaired electrons in each canonical structure must be the same. These two paired electrons would, therefore, form a long bond as shown by dotted line in (V). The distance between them being too large, the bond is not effective one and is termed a *formal bond.*

Thus the most important contribution to resonance hybrid is made by structure (I) and the resonance energy is expected to be small. It is found to be 14·64 kJ mol^{-1}. Thus in 1,3-butadiene the two terminal double bonds have very small single bond character and the central single bond has a very small double bond character.

(*ii*) **Due to Delocalisation of Electrons.** This has been discussed on page 1·101.

(*iii*) **Due to Variation in Bond Energies.** More recently it has been suggested that greater stability of conjugated alkadienes is not due to resonance stabilisation or delocalisation of electrons. It is now believed to be due to variation in bond energies arising from the difference in the hybrid state of the carbon atom. Some bond lengths and bond energies are given below for ready reference.

Bond type	*Bond length* (Å)	*Bond energy* (*kJ mol*$^{-1}$)
C(sp^3)—C(sp^3)	1·54	346·3
C(sp^3)—C(sp^2)	1·50	357·5
C(sp^3)—C(sp)	1·46	382·5
C(sp^2)—C(sp^2)	1·48	383·2
C(sp^2)—C(sp)	1·43	403·7
C(sp)—C(sp)	1·38	433·5

$C(sp^3)—H$	1·11	412·8
$C(sp^2)—H$	1·10	412·9
$C(sp)—H$	1·08	428·4
$C(sp^2)=C(sp^2)$	1·34	598·7

TEST YOUR UNDERSTANDING

1. *The greater the number of alkyl groups attached to the doubly bonded carbon atoms, the more stable the alkene.* Give the name of this rule and with its help arrange the following alkenes in the order of (*a*) Decreasing stability, and (*b*) decreasing ease of formation.

$R_2C=CR_2$; $R_2C=CH_2$; $CH_2=CH_2$; $R_2C=CHR$; $RCH=CHR$; $RCH=CH_2$.

2. Give structures of various alkenes expected from dehydrohalogenation of (*a*) 1-chloropentane ; (*b*) 2-chloropentane ; (*c*) 3-chloropentane ; (*d*) 2-chloro-2-methylbutane ; (*e*) 3-chloro-2-methylbutane ; (*f*) 2-chloro-2,3-dimethylbutane ; (*g*) 1-chloro-2, 2-dimethylpropane. Predict the major product in each case.

3. What alkyl halide, if any, would yield each one of pure alkene upon dehydrohalogenation ?

(*a*) Isobutylene ; (*b*) 1-pentene ; (*c*) 2-pentene ; (*d*) 2-methyl -1-butene ; (*e*) 2-methyl-2-butene.

4. Stability of the carbocations is in the order :

Allyl or tertiary > secondary > primary > $CH_3^{\oplus}$

More stable the carbocation, more readily it is formed. A carbocation undergoes rearrangement to give a more stable carbocation.

Keeping these facts in mind, explain the formation of 2-Butene on dehydration of 1-butanol.

5. Predict the major product of dehydration of each of the following :

(*a*) $(CH_3)_2C(OH).CH_2.CH_3$; (*b*) $(CH_3)_2.CH.CHOH.CH_3$;
(*c*) $(CH_3)_2C(OH).CH(CH_3)_2$.

6. (*a*) What is the acid (*i*) in an aqueous solution of HBr, and (*ii*) in dry HBr ?

(*b*) Which is the stronger acid in the above ?

(*c*) Which can better transfer hydrogen ion to an alkene ?

7. *Electrophilic addition to a carbon-carbon double bond involves the intermediate formation of the more stable carbocation.* Which rule is replaced by this general rule ?

8. Addition of HCl to 3-methyl-1-butene yields mixture of two alkyl-chlorides. What are they likely to be and how is each formed ?

9. Free-radical addition to a carbon-carbon double bond involves the intermediate formation of the more stable free radical. The stability of free radicals is in the order :

allyl > tertiary > secondary > primary > $CH_3\cdot$ > vinyl

Keeping these facts in mind

(*a*) formulate the addition of Br_2 to propylene and addition of HBr to the resulting free radical, and

(*b*) explain the action of Cl_2 on propylene at 800-900K.

10. Identify A, B, C, D, and E in the following assuming that various possibilities are : alkane, alkene, alkyl halide, secondary and tertiary alcohol.

Compound	Extra elements detected	Solubility in H_2SO_4	Br_2/CCl_4	$KMnO_4$	CrO_3
A	—	Insoluble	—	—	—
B	—	Soluble	—	—	+
C	Cl	Insoluble	—	—	—
D	—	Soluble	+	+	—
E	—	Soluble	—	—	—

11. When HCl is added to acrolein, $CH_2=CH.CH=O$, the addition occurs contrary to Markownikoff's rule to give $ClCH_2.CH_2.CH=O$. Explain.

12. Isobutylene in the presence of H_2SO_4 forms a mixture of two isomeric alkenes, C_8H_{16}. Formulate the reaction. How would you distinguish between the isomers chemically ?

13. **Draw the energy profiles for the reactions :**

(*i*) $MeCH=CH_2 + HX \longrightarrow MeCH_2.CH_2\oplus + X^-$

(*ii*) $MeCH=CH_2 + HX \longrightarrow Me\overset{\oplus}{C}HMe + X^-$

Give reasons.

KEY

1. $R_2C=CR_2 > R_2C=CHR > R_2C=CH_2$, $RCH=CHR > RCH=CH_2$
2. (*g*) gives none.
5. (*a*) $(CH_3)_2\,C=CH.\,CH_3$; (*b*) $(CH_3)_2C=CH.CH_3$;
   (*c*) $(CH_3)_2C=C(CH_3)_2$.
6. (*a*) (*i*) $H_3\overset{+}{O}$; (*ii*) HBr ; (*b*) HBr ; (*c*) HBr.
7. Markownikoff's rule.

10. A is alkane ; B is secondary alcohol ; C is alkyl halide ; D is alkene ; E is tertiary alcohol.

11. It is a conjugated system and as in the case of conjugated diene addition at the end is preferred resulting in the formation of resonance-stabilised carbocation.

$$CH_2=CH—CH=O + H^+ \longrightarrow \underbrace{CH_2\cdots CH\cdots CH}_{\oplus}—OH \text{ or } CH_2—\underbrace{CH\cdots CH\cdots O}_{\oplus}$$

More stable as positive charge is carried by carbon atoms alone

Less stable as positive charge is carried partly by highly electro-negative oxygen atom

$$\underbrace{CH_2\cdots CH\cdots CH}_{\oplus}—OH \xrightarrow{Cl^-} \underset{\displaystyle Cl}{CH_2}—CH=CH—OH \rightarrow CH_2Cl—CH_2—CH=O$$

Enol form Keto form

12. $$Me_2C=CH_2 \xrightarrow{H^+} Me_3C\oplus \; CH_2=CMe_2 \longrightarrow$$

$$Me_3C—CH_2—\overset{\oplus}{C}Me_2 \xrightarrow{-H^+} Me_3C—CH=CMe_2 + Me_3C—CH_2—CMe=CH_2$$

Distinguish by ozonolysis.

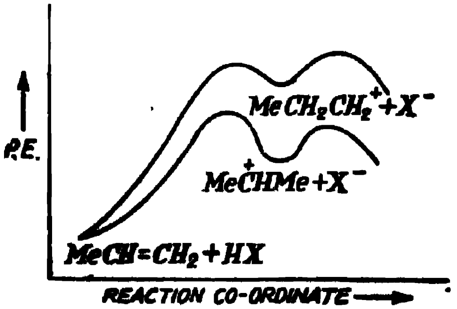


Fig. 14·11.

13. $Me\overset{+}{C}H_2Me$ (2° carbocation) is more stable than $MeCH_2CH_2^+$(1° carbocation). The former has lower energy level.

E_{act} for reaction (*i*) is therefore less than that for reaction (*ii*). This is depicted in the energy profile (Fig. 14·11).

QUESTIONS

A. **Essay Type :**

1. (*a*) What happens when propylene is treated separately with HBr and HOCl (*i*) in presence of, and (*ii*) in absence of peroxides ? State the rule involved in these reactions.

(*b*) Discuss the structural formula of ethylene. (*Delhi B.Sc. Hons. Sub. 1976*)

2. Give the preparation and properties of ethylene. Explain electrophilic additions to it by halogens. (*Jammu B.Sc. 1977*)

3. Write a note on Baeyer's strain theory along with Sachse and Mohr Theory of strainless rings. (*Guru Nanak Dev B.Sc. 1977 ; Kerala 1975*)

4. (*a*) What products are obtained when the following compounds undergo mono-substitution :

(*i*) Propane, and (*ii*) Propylene ?

(*b*) Give examples of two different kinds of addition products when propylene reacts with HBr under different conditions. (*Delhi B.Sc. Hons. Sub. 1977*)

5. What is ozonolysis ? Taking at least one example of an olefin, explain as to how it helps in the location of a double bond. (*Delhi B.Sc. Hons. 1977*)

6. Give the mechanism of the following reactions :

(*i*) Dehydration of alcohols. (*ii*) Dehydrohalogenation.

(*iii*) Peroxide effect. (*iv*) Alkylation of alkenes. (*Guru Nanak Dev B.Sc. 1977 ; Jabalpur 1976*)

7. Enumerate and discuss various methods available for the preparation of alkenes. Give the properties and uses of ethylene.

8. (*a*) How is ethylene prepared in the laboratory ? How does it react with bromine water, (*b*) conc. sulphuric acid, (*c*) hydrogen chloride, (*d*) acidified potassium permanganate, (*e*) hypochlorous acid, and (*f*) ozone ?

9. Give evidence in support of the double bond formula of ethylene. Name the compounds and indicate the conditions under which they are formed when propylene is treated with (*a*) bromine, (*b*) hydrogen bromide, (*c*) hypochlorous acid, (*d*) ozone, and (*e*) conc. H_2SO_4.

10. Write a short note on :

(*a*) "Detection and location of double bonds." (*Delhi B.Sc. 1971*)

(*b*) Mechanism for hydration of olefins. (*Punjab B.Sc. 1970*)

11. (*a*) What are alkadienes ? Name two important alkadienes and state their importance in industry.

(*b*) Give the preparation and properties of Butadiene. (*Delhi B.Sc. 1971*)

12. Write an essay on Thiele's theory of partial valency.

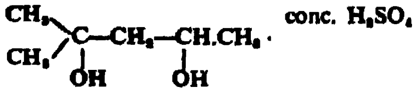
13. Complete the following reactions :

(*a*) $CH_3CH_2.CH{=}CH_2 + HCl \longrightarrow$

(*b*) $(CH_3)_3CH + (CH_3)_2C{=}CH_2 \xrightarrow{\text{Cold conc. } H_2SO_4}$

(*c*) $CH_3.CH{=}CH_2 + HOCl \longrightarrow$

(*d*)



$$(CH_3)_2\underset{\substack{|\\ OH}}{C}{-}CH_2{-}\underset{\substack{|\\ OH}}{CH}.CH_3 \cdot \quad \text{conc. } H_2SO_4$$

(*e*) $(CH_3)_2C{=}CH_2 \xrightarrow{\text{conc. } H_2SO_4}$

14. How will you prepare the following :

(*a*) Propane from *n*-propyl alcohol. (*b*) *n*-Propyl bromide from propene.

(*c*) 1-Butene from 1, 2-dichlorobutane.

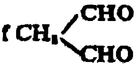
(*d*) Allyl chloride from propene. (*e*) Glycol from ethylene.

15. Write down the structural formulae of olefins from which the following products are obtained on ozonolysis :

(*a*) Ethyl methyl ketone and propionaldehyde.

(*b*) One molecule of pyruvaldehyde ($CH_3CO.CHO$) and two molecules of formaldehyde.

(*c*) Cyclopentanone and acetone. (*d*) Formaldehyde only.

(*e*) Two molecules of 
$CH_2(CHO)_2$ (*f*) 2, 6-Heptanediene.

(*g*) Ethyl methyl ketone and acetaldehyde.

16. What is peroxide effect ? Explain the mechanism of peroxide initiated addition of hydrobromic acid on propylene. Why is peroxide effect not shown by hydrochloric acid ? (*G.N.D. B.Sc. 1976, 75*)

17. Explain the following :

(*i*) Addition of bromine to alkene in a two-step process.

(*ii*) Anti-Markownikoff addition to alkene is possible in case of HBr. (*B.N.C. B.Sc. 1976*)

18. Give the mechanism of allylic substitution in alkenes. (*G.N.D. B.Sc. 1976*)

19. Discuss the mechanism of the following reactions :

(*i*) $>C=C<+Br_2+AlBr_3$ (addition).

(*ii*) Dehydration of alcohols.

(*iii*) Dehydrohalogenation of alkyl halides.

(*iv*) Formation of halohydrins. (*Punjab B.Sc. 1976*)

20. Give the structure of alkenes that yield on ozonolysis

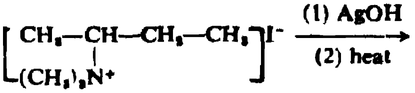
(*i*) only acetone

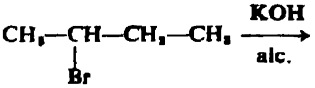
(*ii*)
$CH_3—CH(CH_3)—CHO$ and CH_3CHO

What would each of these alkenes yield upon cleavage by $KMnO_4$? (*Punjab B.Sc. 1976 Supp.*)

B. Short Answer Type :

1. Complete the following reactions. Giving reasons in support of your answer, assign the structure to the main product formed in each case :

(*i*) 
$[CH_3—CH(N^+(CH_3)_3)—CH_2—CH_3]I^- \xrightarrow[\text{(2) heat}]{\text{(1) AgOH}}$

(*ii*) 
$CH_3—CH(Br)—CH_2—CH_3 \xrightarrow[\text{alc.}]{\text{KOH}}$

(*iii*) $(CH_3)_3C—CH_2\ Br \xrightarrow{\text{KOH}}$ (*Delhi B.Sc. Hons. 1980, 76*)

2. State and illustrate the rule which governs the addition of HBr to propylene. (*Delhi B.Sc. 1976*)

3. Account for the fact : Addition of bromine to ethylene in the presence of NaCl gives not only $BrCH_2.CH_2Br$ but also $BrCH_2.CH_2Cl$. (*Kerala B.Sc. 1975*)

4. Explain briefly why butadiene gives 1, 2 and 1, 4 addition products. (*Delhi B.Sc. Hons 1976 ; B.Sc. 1977*)

5. Why is the chair form of cyclohexane more stable than the boat form ? Make diagrams of both forms. (*Delhi B.Sc. Hons. 1976*)

6. Give chemical tests to distinguish between 1-Butene and 2-Butene. (*Delhi B.Sc. 1976 ; B.Sc. Hons. 1976*)

7. Write a note on Markownikoff's rule. (*Delhi B.Sc. 1977*)

8. Write a note on mechanism of addition of bromine to ethylene. (*Delhi B.Sc. 1977*)

9. Predict the products formed :

(*i*) $CH_3.CH_2.CH_2.CH_2OH \xrightarrow[\Delta\ (140^\circ)]{\text{conc } H_2SO_4}$

(*ii*) $CH_3.CH=CH_2 \xrightarrow{\text{HOCl}}$ (*Delhi B.Sc. Hons Sub. 1977*)

10. Name the following :

(*a*) $(CH_3)_2\ C=CH_2$. (*b*) $(CH_3)_2\ C=CHC_2H_5$.

(*c*) $CH_3.CH=CH.CH_3$. (*d*) $(CH_3)_2\ CH.CH=CH.CH_3$.

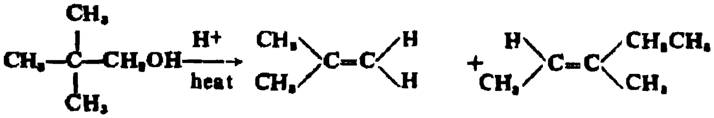
(*e*) $CH_3.CH_2.CH_2C(=CHCH_3)\ CH_2.CH=CH_2$.

11. Write structural formulae for :

(*a*) 4-ethyl-5-methyl-2-hexene. (*b*) 2, 3-diethyl-1, 3-butadiene.
(*c*) Trimethylethylene or 2-Methyl-2-butene.
(*d*) 3, 5-octadiene. (*e*) 3-methyl-1-butene.

12. Which compound would you expect to have large heat of hydrogenation (in kJ mol^{-1}) *cis*-cyclooctene or *trans* cyclooctene ?

13. Write step-by-step mechanisms that account for each product of the following reactions and explain the relative proportions of the isomers obtained.

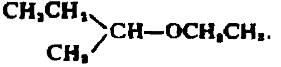

(*major product*) (*minor product*)

14. Show all steps in the acid-catalysed hydration of propene. Explain why the product is 2-propanol and not 1-propanol.

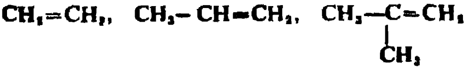
15. Give the structure and name of the product obtained on addition of I-Cl to propene.

16. Write all steps of mechanism for the acid catalyzed dimerisation of propene. What would be the major product ?

17. When 2-Butene is treated with hydrogen chloride in ethanol, one of the products of the reaction is $(CH_3CH_2)(CH_3)CH-OCH_2CH_3$. Write mechanism to account for this product.

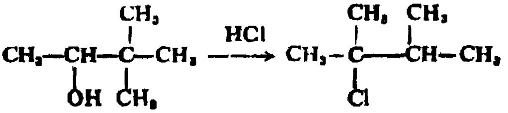


18. Arrange the following alkenes in order of reactivity toward acid-catalyzed hydration and explain with reasoning.



$$CH_2{=}CH_2,\quad CH_3-CH{=}CH_2,\quad CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2$$

19. Write a mechanism that explains the course of the following reaction :



20. The relative rates of addition of hydrogen chloride to the following alkenes increase in the order below :

Ethene < propene < 2-Butene < 2-Methylpropene

Explain.

21. Explain the following equations :

(*i*) $CH_3-CH{=}CH_2 \xrightarrow[770\ K]{Cl_2}$

(*ii*) $CH_3CHCl\,CH_2CH_3 \xrightarrow[EtOH]{OH^-}$

(*Delhi B.Sc. Hons. Sub. 1978*)

22. Discuss the mechanism of addition of HBr to propene.
(*Andhra B.Sc. 1978*)

23. Discuss the mechanism of free radical addition to conjugated dienes. (*Punjab B.Sc. 1971*)

24. Explain, with a suitable reaction, the mechanism of 1, 4 addition.
(*Punjab B.Sc. 1972*)

25. What is meant by 1, 4 and 1, 2 electrophilic addition to conjugated dienes. Explain the reaction mechanism involving these additions by selecting suitable examples. How does temperature affect the rate of these reactions ? Explain. (*Punjab B.Sc. 1975*)

26. Explain Electrophylic Addition to 1, 3-butadiene. What is the effect of temperature on the addition of bromine to this compound ? (*B.N.C. B.Sc. 1976*)

27. On the basis of reaction mechanism give the structures of the chief product or products expected by the action of $Br.CCl_3$ in the presence of peroxide on :

(*i*) 1, 3-butadiene (*ii*) 1, 3-pentadiene
(*iii*) 1, 4-pentadiene (*iv*) 2-methyl-1, 3-butadiene.
(*Punjab* B.Sc. *1976* *Supp.*)

28 Addition of hydrogen choride, hydrogen bromide and hydrogen iodide to propene leads to the formation of corresponding isopropyl halides. In the presence of peroxides addition of hydrogen bromide gives *n*-propyl bromide and of hydrogen chloride gives isopropyl chloride but with hydrogen iodide only iodine is liberated and no appreciable addition reaction takes place. Given that the bond strengths of the hydrogen halides are as HCl>HBr>HI, suggest an explanation for these observations. (*Delhi B.Sc. Hons. I Year 1972*)

C. Problems :

1. An alkene X on ozonolysis, gives $CH_3.CH_2.CHO$ and HCHO. What is the structure of X ? What products would it form, if it is oxidised with acidic potassium permanganate solution ? (*Delhi B.Sc. Hons. Sub. 1977*)

2. On ozonolysis followed by reduction an organic compound C_7H_{14} (A) gives an aldehyde C_3H_6O (B) and a ketone C_4H_8O (C). Identify the compounds A, B and C. Express the above reactions by means of equations.

3. Write down the structures of the compounds A and B on the basis of the following data : (*i*) A and B both yield normal butane on reduction with zinc-copper couple. (*ii*) When refluxed with sodium and ether, A yields normal octane while B yields 3, 4-dimethylhexane.

4. An unsaturated hydrocarbon A on hydration gave an alcohol B. Oxidation of B gave ketone C. When the hydrocarbon A was submitted to ozonolysis it gave formaldehyde and propionaldehyde. What formulae would you assign to A, B and C ? Give the reactions involved.

5. An unsaturated hydrocarbon of the formula C_8H_{14} on hydrogenation absorbed two molecules of hydrogen. On oxidation it yields one molecule each of acetic acid, malonic acid and acetone. Give the structure of the hydrocarbon.

6. A hydrocarbon of the formula C_9H_{16} absorbs two molecules of hydrogen when hydrogenated. On oxidation it gives one molecule each of acetic acid, propionic acid and acetoacetic acid. Deduce the structure of the hydrocarbon.

7. On reduction of compound C_6H_{10} (A) gives first C_6H_{12} (B) and finally C_6H_{14} (C). On ozonolysis followed by reduction (A) gives two aldehydes C_2H_4O (D) and $C_2H_2O_2$ (E). Oxidation of (B) with acidified potassium permanganate gives the acid $C_3H_4O_2$ (F). Identify the compounds A to F and express various reactions involved by means of equations.

8. A pure hydrocarbon of the formula C_5H_{10} decolorises bromine solution. It dissolves in concentrated sulphuric acid and yields 2-methylbutane on hydrogenation. On oxidation with potassium permanganate it yields one molecule of acetone and one molecule of acetic acid. Derive the structural formula of the hydrocarbon from the above data.

9. Bromination of an organic compound of formula C_6H_{12} yields $C_6H_{12}Br_2$. On reduction the compound gives 2-methylpentane. On oxidation it yields a mixture of acetic and isobutyric acids. Assign a structural formula to the organic compound and give its IUPAC name. Express the above reactions by means of chemical equations.

10. A pure hydrocarbon of the formula C_6H_{12} decolorises bromine solution, dissolves in concentrated sulphuric acid, yields 2-methylpentane on hydrogenation and on ozonolysis gives formaldehyde and 3-methylbutanal.

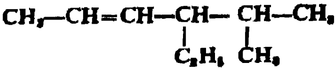
Give the structural formula of the above compound and formulate the above reactions. (*Delhi B.Sc. 1971*)

11. A compound A, C_4H_9Br, on treatment with alcoholic KOH, gave compound B, C_4H_8. Treatment of B with ozone followed by reduction yielded $CH_3CH{=}O$ as the only product. What two possible structures for B account for these facts ? What is the structure of A ?

ANSWERS

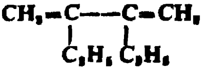
B. 10. (*a*) 2-methyl-1-propene. (*b*) 2-methyl-2-pentene. (*c*) 2-Butene. (*d*) 4 Methyl-2-pentene. (*e*) 4-propylhexa-1, 4-diene.

11. (*a*)



$CH_3{-}CH{=}CH{-}\underset{C_2H_5}{CH}{-}\underset{CH_3}{CH}{-}CH_3$

(*b*)

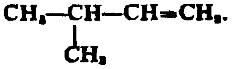


$CH_3{=}\underset{C_2H_5}{C}{-}\underset{C_2H_5}{C}{=}CH_2$

(*c*) $(CH_3)_2C{=}CH.CH_3$.

(*d*) $CH_3{-}CH_2{-}CH{=}CH{-}CH{=}CH{-}CH_2{-}CH_3$.

(*e*)



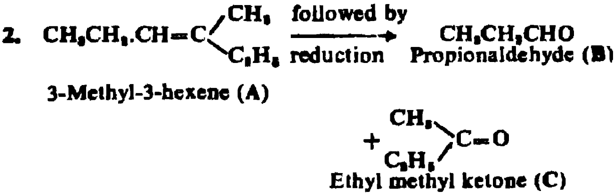
$CH_3{-}\underset{CH_3}{CH}{-}CH{=}CH_2$.

C. 1. X is $CH_3.CH_2.CH{=}CH_2$ (1-Butene).

$\xrightarrow[KMnO_4]{acid}$ CH_3CH_2COOH + HCOOH

Propionic acid Formic acid

2.



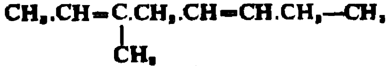
$$CH_3CH_2.CH{=}C\begin{matrix}CH_3\\C_2H_5\end{matrix} \xrightarrow[\text{reduction}]{\text{Ozonolysis followed by}} \underset{\text{Propionaldehyde (B)}}{CH_3CH_2CHO} + \underset{\text{Ethyl methyl ketone (C)}}{\begin{matrix}CH_3\\C_2H_5\end{matrix}\!\!>C{=}O}$$

3-Methyl-3-hexene (A)

3. *A* is $CH_3.CH_2.CH_2.CH_2X$ (1-Halogenobutane).
B is $CH_3.CH_2.CHX.CH_3$ (2-Halogenobutane).

4. *A* is $CH_3.CH_2.CH{=}CH_2$ (1-Butene)
B is $CH_3.CH_2CHOH.CH_3$ (2-Butanol)
C is $CH_3.CH_2.CO.CH_3$ (Butanone)

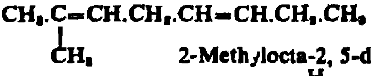
5.



$CH_3.CH{=}\underset{CH_3}{C}.CH_2.CH{=}CH.CH_2{-}CH_3$

3-Methyl-2, 5-octadiene

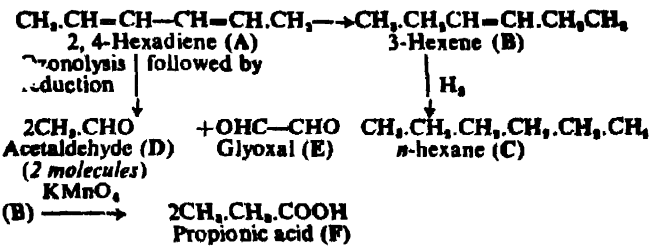
6.



$CH_3.\underset{CH_3}{C}{=}CH.CH_2.CH{=}CH.CH_2.CH_3$

2-Methylocta-2, 5-diene

7.



$$\underset{\text{2, 4-Hexadiene (A)}}{CH_3.CH{=}CH{-}CH{=}CH.CH_3} \xrightarrow{H_2} \underset{\text{3-Hexene (B)}}{CH_3.CH_2CH{=}CH.CH_2CH_3}$$

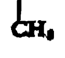
Ozonolysis followed by reduction ↓ (A); H_2 ↓ (B)

$\underset{\text{Acetaldehyde (D)}}{2CH_3.CHO}$ + $\underset{\text{Glyoxal (E)}}{OHC{-}CHO}$ $\underset{n\text{-hexane (C)}}{CH_3.CH_2.CH_2.CH_2.CH_2.CH_3}$

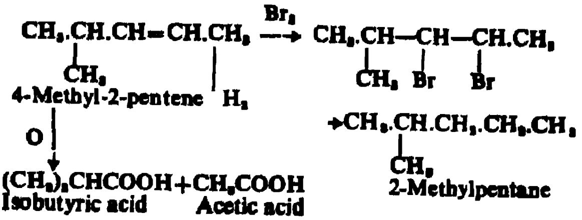
(*2 molecules*)

$(B) \xrightarrow{KMnO_4} \underset{\text{Propionic acid (F)}}{2CH_3.CH_2.COOH}$

8.



$CH_3{-}\underset{CH_3}{C}{=}CH{-}CH_3$ (2-Methyl-2-butene)

9. 

$$CH_3.\underset{CH_3}{\underset{|}{C}}H.CH=CH.CH_3 \xrightarrow{Br_2} CH_3.\underset{CH_3}{\underset{|}{C}}H-\underset{Br}{\underset{|}{C}}H-\underset{Br}{\underset{|}{C}}H.CH_3$$

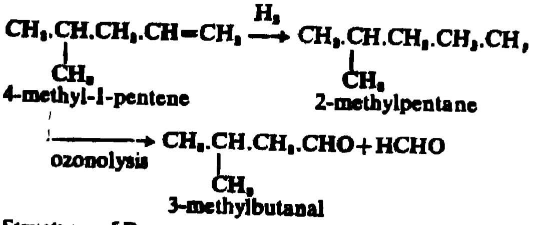
4-Methyl-2-pentene

$$\xrightarrow{H_2} CH_3.\underset{CH_3}{\underset{|}{C}}H.CH_2.CH_2.CH_3$$

2-Methylpentane

$$\xrightarrow{O} (CH_3)_2CHCOOH + CH_3COOH$$

Isobutyric acid Acetic acid

10. 

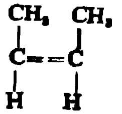
$$CH_3.\underset{CH_3}{\underset{|}{C}}H.CH_2.CH=CH_2 \xrightarrow{H_2} CH_3.\underset{CH_3}{\underset{|}{C}}H.CH_2.CH_2.CH_3$$

4-methyl-1-pentene 2-methylpentane

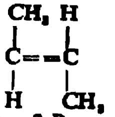
$$\xrightarrow[\text{ozonolysis}]{} CH_3.\underset{CH_3}{\underset{|}{C}}H.CH_2.CHO + HCHO$$

3-methylbutanal

11. *Structure of* B



cis-2-Butene



trans-2-Butene

Structure of A

$CH_3-CH_2-CHBr-CH_3$ (2-Bromobutane)

15

Alkynes or Acetylenes

1. The Acetylenes.—The unsaturated hydrocarbons that contain one carbon-carbon triple bond are called *Acetylenes* or *alkynes* and have the general formula C_nH_{2n-2}. Acetylene, $CH \equiv CH$ being the simplest alkyne, the homologous series is referred to as the **Acetylene series.** The triple bond is also known as the *acetylenic bond.*

2. Nomenclature.—Higher homologues are named either as derivatives of acetylene or after the corresponding paraffins (*IUPAC system*) by changing the suffix *-ane* into *-yne*. The rules of numbering the carbon atoms are the same as for olefins. The names of a few homologues are given below :

Formula	*Corresponding paraffin*	*Common name*	*IUPAC name*
C_nH_{2n-2}	C_nH_{2n+2} *Alkanes*	Acetylenes	Alkynes
$CH \equiv CH$	C_2H_6 *Ethane*	Acetylene	Ethyne
$CH_3.C \equiv CH$	C_3H_8 *Propane*	Methylacetylene or Allylene	Propyne
$CH_3.C \equiv C.CH_3$	C_4H_{10} *Butane*	Dimethylacetylene or β-Crotonylene	2-Butyne
$CH_3CH_2C \equiv CH$		Ethylacetylene or α-crotonylene	1-Butyne

IUPAC system is more convenient for naming higher members.

ACETYLENE OR ETHYNE, C_2H_2

3. Occurrence.—It does not occur freely in nature. Traces of acetylene are present in coal gas (about 0·06%) and gases produced by incomplete combustion of coal gas and other organic substances like alcohol and hydrocarbons. For instance, when a Bunsen burner strikes back, the issuing gas contains about 0·8% of acetylene.

4. Preparation.—(*i*) *By the action of water on calcium carbide.** Acetylene is prepared in the laboratory by this method

$$\underset{\text{Calcium carbide}}{CaC_2} + 2H_2O \longrightarrow Ca(OH)_2 + \underset{\text{Acetylene}}{C_2H_2}$$

Lumps of calcium carbide are placed on a layer of sand in a flask fitted with a dropping funnel and a delivery tube (Fig. 15·1). *The air of the flask is displaced with oil gas as acetylene forms an*

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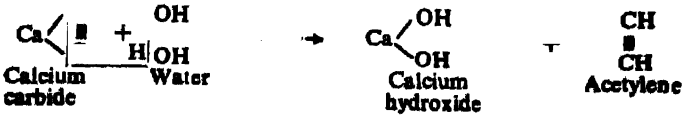
* To explain the tetravalency of carbon and divalency of calcium in CaC_2 the equation can be written as below :



explosive mixture with air. Water is dropped from the dropping funnel and acetylene evolved is collected over water.

Acetylene prepared by this method is not pure but contains small amounts of phosphine, hydrogen sulphide, arsine, ammonia, etc. The impurities depend upon the purity of calcium carbide used. The gas is purified by bubbling it through acidified copper sulphate, acidified dichromate or bleaching powder solution. Whereas other impurities are dissolved in water or react with the acid, phosphine is retained as copper phosphide or phosphoric acid.

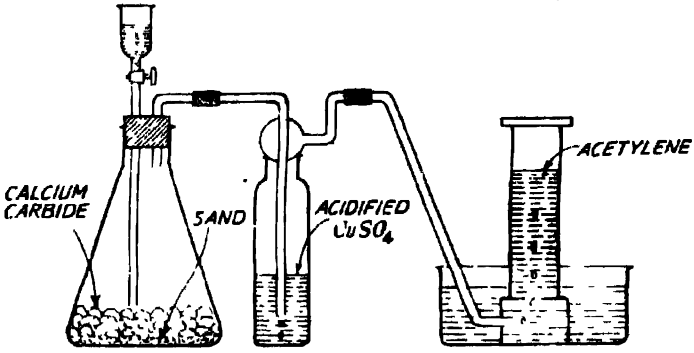
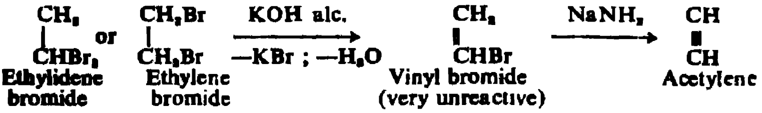


Fig. 15 1—Preparation of acetylene.

(*ii*) *By dehydrohalogenation of dihalides in two stages* :

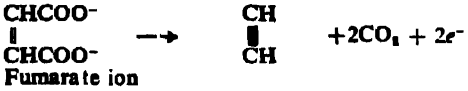


$$\underset{\text{Ethylidene bromide}}{\begin{matrix}CH_3\\ |\\ CHBr_2\end{matrix}} \text{ or } \underset{\text{Ethylene bromide}}{\begin{matrix}CH_2Br\\ |\\ CH_2Br\end{matrix}} \xrightarrow[-KBr\ ;\ -H_2O]{KOH\ alc.} \underset{\substack{\text{Vinyl bromide}\\ \text{(very unreactive)}}}{\begin{matrix}CH_2\\ \|\\ CHBr\end{matrix}} \xrightarrow{NaNH_2} \underset{\text{Acetylene}}{\begin{matrix}CH\\ |||\\ CH\end{matrix}}$$

The vinyl halide obtained in first stage is very unreactive, use of a stronger base is, therefore, required for dehydrohalogenation in the second stage.

(*iii*) *By the electrolysis of a concentrated solution of sodium or potassium salt of maleic or fumaric acid* (**Kolbe's reaction**).

At anode:



$$\underset{\text{Fumarate ion}}{\begin{matrix}CHCOO^-\\ \|\\ CHCOO^-\end{matrix}} \longrightarrow \begin{matrix}CH\\ |||\\ CH\end{matrix} + 2CO_2 + 2e^-$$

At cathode :

$$2H_2O + 2e^- \longrightarrow 2OH^- + H_2\uparrow$$

(*iv*) *By heating a trihalogen derivative of methane with silver powder, e.g.*, by heating iodoform with silver powder.

$$\underset{\text{Iodoform}}{CH}\boxed{I_3+6Ag+I_3}\underset{\text{Iodoform}}{CH} \longrightarrow \underset{\text{Acetylene}}{CH\equiv CH} + 6AgI$$

5. **Manufacture.**—(*i*) Laboratory method of preparation of acetylene from calcium carbide is also used industrially since

calcium carbide is readily manufactured by heating calcium oxide with coke in an electric furnace and is quite cheap.

$$CaO+3C \xrightarrow{2800\text{-}3100K} CaC_2+CO$$

Acetylene needed for welding purposes by oxy-acetylene flame is prepared on the spot by an automatic plant (Fig. 15·2). Calcium carbide is placed in a cage fitted in a gas holder which floats in water placed in an iron tank. Calcium carbide reacts with water to give acetylene. As more and more of the gas collects, the gas holder rises till the cage goes out of water. As the acetylene stored is used up, the gas holder again comes down and the reaction starts

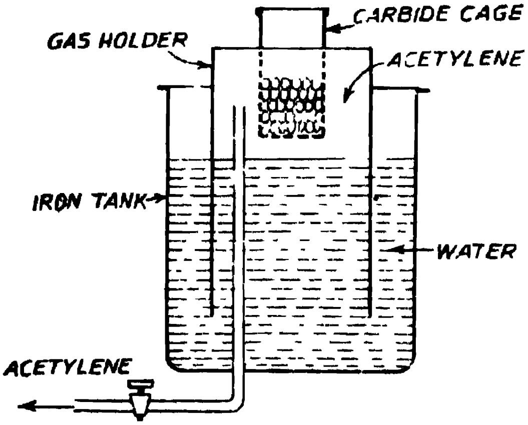


Fig. 15·2—Automatic plant for preparation of acetylene needed industrially for welding purposes.

(*ii*) A more recent method for the manufacture of acetylene is based on petroleum. This involves the controlled partial oxidation of methane at high temperature.

$$6CH_4+O_2 \xrightarrow{1800K} 2HC\equiv CH+2CO+10H_2$$

CO and H_2 obtained as by-products are used in the manufacture of methanol.

6. **Synthesis.** – Berthelot synthesised acetylene from its elements by striking an electric arc between two carbon electrodes in an atmosphere of hydrogen gas and the method is known after his name as *Berthelot synthesis*. The method is of no practical utility and is of academic interest only.

$$2C+H_2 \rightleftharpoons C_2H_2$$

7. **Properties : Physical.**—It is a colourless gas with sweet smell when pure. The characteristic garlic odour usually associated with acetylene is due to phosphine present as impurity. It is slightly lighter than air, sparingly soluble in water, but very soluble in alcohol and acetone under pressure. It liquefies at 189K under ordinary pressure Liquid acetylene is dangerously explosive hence use or storage of liquid acetylene is prohibited by law. For transportation, acetylene is dissolved under high pressure in acetone soaked on porous material packed in steel cylinders. It is somewhat poisonous in nature.

The IR absorption region of alkynes depends on whether these contain acetylenic hydrogen or not. For example in RC≡CH, there is absorption in the region 3310−3300 cm^{-1} (m) due to the ≡C—H stretch and in the region 2140-2100 cm^{-1} (w) due to the C≡C stretch. In alkynes of the formula RC≡CR the absorption region for C≡C stretch is 2260−2190 cm^{-1}(v).

Since electronegativities of C_2H_6, C_2H_4 and C_2H_2 are in the order : $C_2H_2 > C_2H_4 > C_2H_6$, it is expected that chemical shifts of protons should be in this order. However, in actual practice these have been found to be in the following order :

$$C_2H_4(\delta \sim 5 \text{ ppm}) > C_2H_2(\approx 2{\cdot}5) > C_2H_6(\delta \sim 0{\cdot}9)$$

This can be accounted for on the assumption that there is a shielding effect operating in acetylene. The shielding effect is much smaller in ethylene.

Chemical. (1) **Burning.** Acetylene forms an explosive mixture with air or oxygen. In an open jar it burns with a smoky flame but in suitably constructed pinhole burners which you often see at a petty stall, it burns brightly emitting dazzling light injurious to eyes. Oxy-acetylene flame gives a temperature of about 3800K.

$$2C_2H_2+5O_2 \longrightarrow 4CO_2+2H_2O$$

Heat of combustion of acetylene is 1305 kJ whereas heat liberated by burning 24 g of carbon and 2 g of hydrogen is only 1074 kJ. This shows that acetylene can decompose into its elements with evolution of heat (231 kJ per mole). This unstable thermodynamic state of the molecule explains the high reactivity of acetylene and its tendency to explode when compressed.

(2) **Electrophilic Addition Reactions.** Carbon-carbon triple bond is a combination of one sigma bond and two pi bonds. *Acetylene undergoes electrophilic addition due to the availability of the loosely held π electrons.* Strangely enough it is found to be less reactive than ethylene towards electrophilic reagents. However, it is more

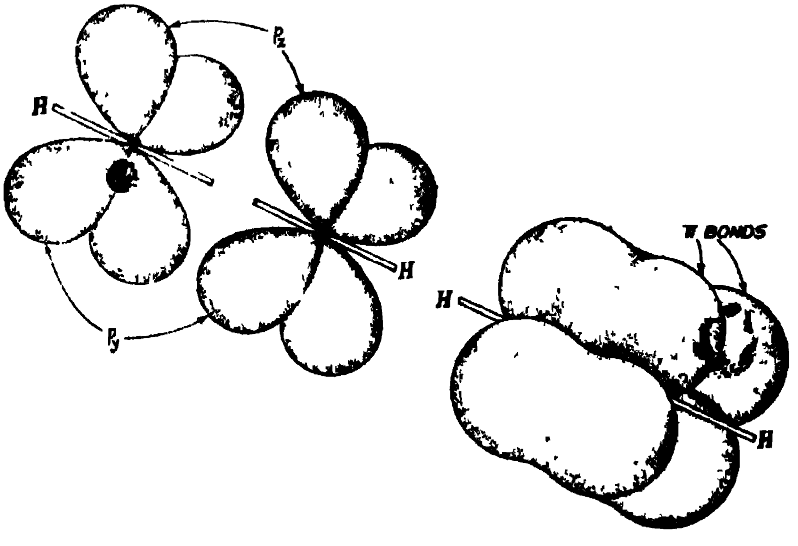
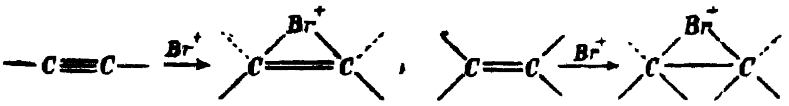


Fig. 15·3—Molecular model for acetylene.

reactive than ethylene towards reagents that are themselves electron rich.

One explanation offered for this strange behaviour is on the assumption that bridged carbocation is obtained as in the case of alkenes. But the one obtained from acetylene is more strained.



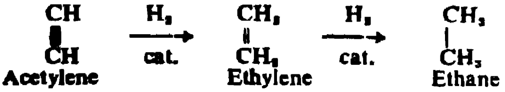
More strained

Dotted lines represent bonds actually present in alkenes and alkanes.

The above assumption may be justified in the light of the fact that products obtained in various addition reactions of acetylene following polar mechanism are stereoselectively *trans*.

It can add up four monovalent atoms or groups in two stages as illustrated by the following reactions. In the first step digonal arrangement changes into the trigonal one which changes further in the second step into the tetrahedral arrangement.

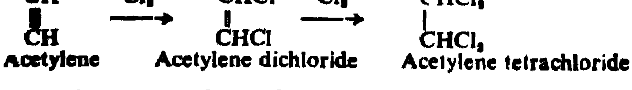
(*i*) ADDITION OF HYDROGEN. Acetylene adds on hydrogen in the presence of a catalyst and the reaction proceeds in two stages :



$$\underset{\text{Acetylene}}{\begin{matrix}CH\\ \| \\ CH\end{matrix}}\ \xrightarrow[\text{cat.}]{H_2}\ \underset{\text{Ethylene}}{\begin{matrix}CH_2\\ \| \\ CH_2\end{matrix}}\ \xrightarrow[\text{cat.}]{H_2}\ \underset{\text{Ethane}}{\begin{matrix}CH_3\\ | \\ CH_3\end{matrix}}$$

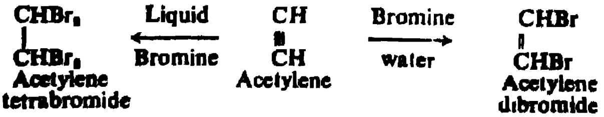
The intermediate product ethylene can be obtained in very good yield if hydrogenation is carried out with a measured amount of hydrogen in the presence of palladium deposited in barium sulphate partially poisoned with quinoline or **Lindlar's Catalyst** (Pd-$CaCO_3$ catalyst poisoned with lead acetate).

(*ii*) ADDITION OF HALOGENS. Gaseous chlorine or bromine adds in the dark to give di- and tetrahalides. The addition is catalysed by light. Acetylenes dihalides when obtained are *trans* isomers.



$$\underset{\text{Acetylene}}{\begin{matrix}CH\\ \| \\ CH\end{matrix}}\ \xrightarrow{Cl_2}\ \underset{\text{Acetylene dichloride}}{\begin{matrix}CHCl\\ \| \\ CHCl\end{matrix}}\ \xrightarrow{Cl_2}\ \underset{\text{Acetylene tetrachloride}}{\begin{matrix}CHCl_2\\ | \\ CHCl_2\end{matrix}}$$

Dilute bromine water gives dibromide whereas tetrabromide is obtained with liquid bromine in the absence of solvent.

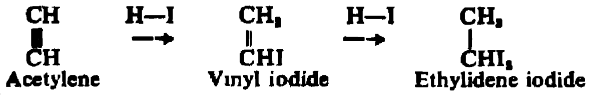


$$\underset{\text{Acetylene tetrabromide}}{\begin{matrix}CHBr_2\\ | \\ CHBr_2\end{matrix}}\ \xleftarrow[\text{Bromine}]{\text{Liquid}}\ \underset{\text{Acetylene}}{\begin{matrix}CH\\ \| \\ CH\end{matrix}}\ \xrightarrow[\text{water}]{\text{Bromine}}\ \underset{\text{Acetylene dibromide}}{\begin{matrix}CHBr\\ \| \\ CHBr\end{matrix}}$$

Acetylene diiodide is obtained with iodine when the reaction is carried out in alcoholic solution.

Tetrahalides when heated with zinc dust regenerate alkynes. ***Bromination is, therefore, used for protecting a triple bond*** in certain reactions.

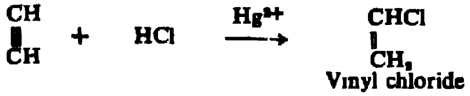
(*iii*) ADDITION OF HALOGEN ACIDS. With halogen acids, addition takes place according to **Markownikoff's rule**—***Negative part of the addendum (molecule to be added) attaches to the least hydrogenated carbon atom***. The order of reactivity is HI>HBr>HCl. The addition can take place in dark but is catalysed by light.



$$\begin{array}{c}\mathrm{CH}\\ |||\\ \mathrm{CH}\end{array} \xrightarrow{\mathrm{H-I}} \begin{array}{c}\mathrm{CH_2}\\ \|\\ \mathrm{CHI}\end{array} \xrightarrow{\mathrm{H-I}} \begin{array}{c}\mathrm{CH_3}\\ |\\ \mathrm{CHI_2}\end{array}$$

Acetylene Vinyl iodide Ethylidene iodide

When acetylene is passed into dilute hydrochloric acid at 340K in the presence of mercuric ions (catalyst), only one molecule is added and we get vinyl chloride.

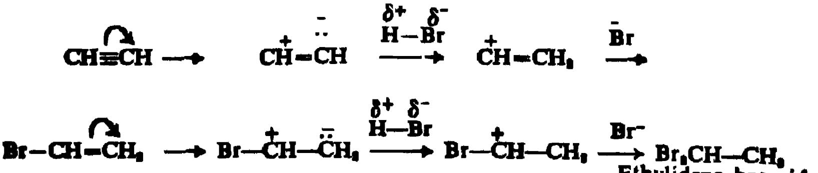


$$\begin{array}{c}\mathrm{CH}\\ |||\\ \mathrm{CH}\end{array} + \mathrm{HCl} \xrightarrow{\mathrm{Hg^{2+}}} \begin{array}{c}\mathrm{CHCl}\\ \|\\ \mathrm{CH_2}\end{array}$$

Vinyl chloride

Peroxides have the same effect on the addition of HBr to acetylene as on olefins (page 1·164).

The mechanism of the addition of halogens and halogen acids is probably the same as that for olefins. For example, addition of HBr to acetylene may be represented as follows :

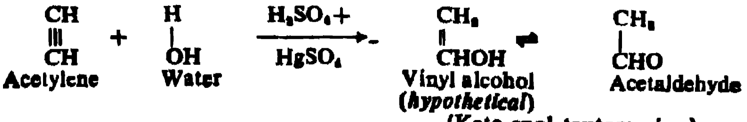


$$\mathrm{CH{\equiv}CH} \longrightarrow \overset{+}{\mathrm{C}}\mathrm{H}{=}\overset{-\,\cdot\cdot}{\mathrm{C}}\mathrm{H} \xrightarrow{\overset{\delta+\ \ \delta-}{\mathrm{H-Br}}} \overset{+}{\mathrm{C}}\mathrm{H}{=}\mathrm{CH_2} \xrightarrow{\overset{-}{\mathrm{Br}}}$$

$$\mathrm{Br{-}CH{=}CH_2} \longrightarrow \mathrm{Br{-}}\overset{+}{\mathrm{C}}\mathrm{H{-}}\overset{-\,\cdot\cdot}{\mathrm{C}}\mathrm{H_2} \xrightarrow{\overset{\delta+\ \ \delta-}{\mathrm{H-Br}}} \mathrm{Br{-}}\overset{+}{\mathrm{C}}\mathrm{H{-}CH_3} \xrightarrow{\mathrm{Br^-}} \mathrm{Br_2CH{-}CH_3}$$

Ethylidene bromide

(*iv*) ADDITION OF WATER. When the gas is passed through 42% sulphuric acid at 330K in presence of 1% mercuric sulphate (*catalyst*) one molecule of water is added up. The mechanism of addition is probably *via* the formation of vinyl alcohol as an intermediate product, which then isomerises to give acetaldehyde.

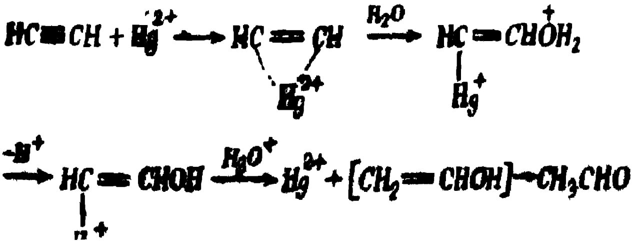


$$\begin{array}{c}\mathrm{CH}\\ |||\\ \mathrm{CH}\end{array} + \begin{array}{c}\mathrm{H}\\ |\\ \mathrm{OH}\end{array} \xrightarrow[\mathrm{HgSO_4}]{\mathrm{H_2SO_4+}} \begin{array}{c}\mathrm{CH_2}\\ \|\\ \mathrm{CHOH}\end{array} \rightleftharpoons \begin{array}{c}\mathrm{CH_3}\\ |\\ \mathrm{CHO}\end{array}$$

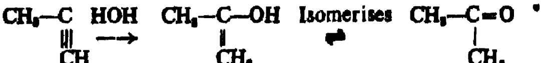
Acetylene Water Vinyl alcohol (*hypothetical*) Acetaldehyde

(Keto-enol tautomerism)

A possible explanation of the function of the catalyst is that Hg^{2+} ion being large sized forms readily a bridged ion (or a π-complex) which then reacts as shown on the next page :



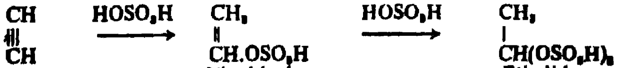
Homologues of acetylene form ketones, *e.g.*, propyne gives acetone.



$$\begin{array}{c}\text{CH}_3\text{—C}\\ |||\\ \text{CH}\end{array} \xrightarrow{\text{HOH}} \begin{array}{c}\text{CH}_3\text{—C—OH}\\ \|\\ \text{CH}_2\end{array} \xrightarrow{\text{Isomerises}} \begin{array}{c}\text{CH}_3\text{—C=O}\\ |\\ \text{CH}_3\end{array}$$

Propyne (*hypothetical*) Acetone

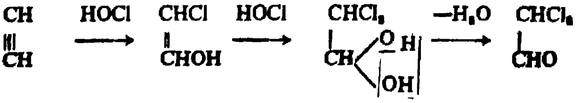
(*v*) ADDITION OF CONC. SULPHURIC ACID. Two molecules of sulphuric acid are added and ethylidene hydrogen sulphate is obtained.



$$\begin{array}{c}\text{CH}\\ |||\\ \text{CH}\end{array} \xrightarrow{\text{HOSO}_2\text{H}} \begin{array}{c}\text{CH}_2\\ \|\\ \text{CH.OSO}_2\text{H}\end{array} \xrightarrow{\text{HOSO}_2\text{H}} \begin{array}{c}\text{CH}_3\\ |\\ \text{CH(OSO}_2\text{H)}_2\end{array}$$

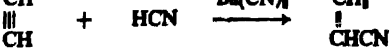
Acetylene Vinyl hydrogen sulphate Ethylidene hydrogen sulphate

(*vi*) ADDITION OF HYPOCHLOROUS ACID. Acetylene when passed into hypochlorous acid solution gives dichloroacetaldehyde.



$$\begin{array}{c}\text{CH}\\ |||\\ \text{CH}\end{array} \xrightarrow{\text{HOCl}} \begin{array}{c}\text{CHCl}\\ \|\\ \text{CHOH}\end{array} \xrightarrow{\text{HOCl}} \begin{array}{c}\text{CHCl}_2\\ |\\ \text{CH(OH)}_2\end{array} \xrightarrow{-\text{H}_2\text{O}} \begin{array}{c}\text{CHCl}_2\\ |\\ \text{CHO}\end{array}$$

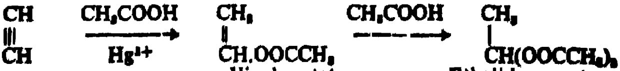
(*vii*) ADDITION OF HCN. Acetylene adds a molecule of hydrogen cyanide in presence of barium cyanide to yield vinyl cyanide.



$$\begin{array}{c}\text{CH}\\ |||\\ \text{CH}\end{array} + \text{HCN} \xrightarrow{\text{Ba(CN)}_2} \begin{array}{c}\text{CH}_2\\ \|\\ \text{CHCN}\end{array}$$

Vinyl cyanide

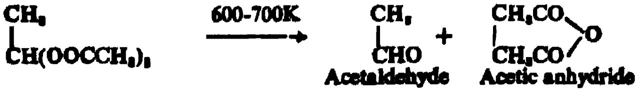
(*viii*) ADDITION OF ACETIC ACID. When acetylene is passed into warm acetic acid in presence of mercuric ions (*catalyst*), vinyl acetate and ethylidene acetate are obtained.



$$\begin{array}{c}\text{CH}\\ |||\\ \text{CH}\end{array} \xrightarrow[\text{Hg}^{2+}]{\text{CH}_3\text{COOH}} \begin{array}{c}\text{CH}_2\\ \|\\ \text{CH.OOCCH}_3\end{array} \xrightarrow{\text{CH}_3\text{COOH}} \begin{array}{c}\text{CH}_3\\ |\\ \text{CH(OOCCH}_3\text{)}_2\end{array}$$

Vinyl acetate Ethylidene acetate

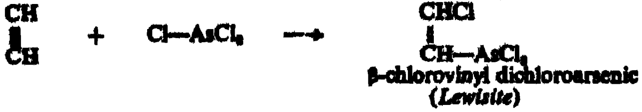
Vinyl acetate is used in the plastic industry. Ethylidene acetate decomposes when heated rapidly to give acetic anhydride and acetaldehyde.



$$CH_3CH(OOCCH_3)_2 \xrightarrow{600\text{-}700K} CH_3CHO + (CH_3CO)_2O$$

Acetaldehyde Acetic anhydride

(*ix*) ADDITION OF ARSENIC TRICHLORIDE. Acetylene adds a molecule of arsenic trichloride to form *Lewisite* (a poisonous gas).



$$CH\equiv CH + Cl{-}AsCl_2 \longrightarrow CHCl{=}CH{-}AsCl_2$$

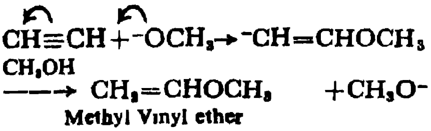
β-chlorovinyl dichloroarsenic (*Lewisite*)

(3) **Nucleophilic Addition Reactions.** Addition of Alcohols. On passing acetylene into methanol at 430-470K in presence of potassium methoxide, and under high pressure to prevent boiling, methyl vinyl ether is obtained. In general alkynes can give addition products (unsaturated ethers) with alcohols.

$$CH\equiv CH + CH_3OH \xrightarrow{CH_3OK} CH_3O.CH{=}CH_2$$

Methyl vinyl ether

The first step in mechanism is believed to be the nucleophilic attack by CH_3O^-



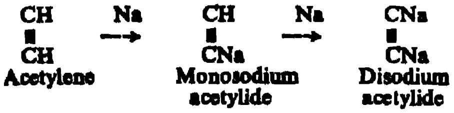
$$CH\equiv CH + {}^-OCH_3 \rightarrow {}^-CH{=}CHOCH_3 \xrightarrow{CH_3OH} CH_2{=}CHOCH_3 + CH_3O^-$$

Methyl Vinyl ether

This is formation of a vinyl compound by addition of a compound containing active hydrogen atom to acetylene and is termed **vinylation.**

(4) **Formation of Acetylides.** The hydrogen atoms in acetylene are acidic in nature. Due to the acidic nature of its hydrogen atoms, acetylene forms metallic derivatives by replacement of one or both hydrogen atoms. For example,

(*i*) Both monosodium and disodium acetylides are formed when acetylene is passed over heated sodium.



$$CH\equiv CH \xrightarrow{Na} CH\equiv CNa \xrightarrow{Na} CNa\equiv CNa$$

Acetylene Monosodium acetylide Disodium acetylide

By using large excess of acetylene the main product is monosodium acetylide. The same product is obtained by passing acetylene into a solution of sodium in liquid ammonia until the blue colour disappears.

Let us consider how strong an acid is acetylene by comparing it with ammonia and water.

$$\underset{\text{Stronger acid}}{HC\equiv CH} + \underset{\text{Stronger base}}{\overset{+}{Na}\overset{-}{NH_2}} \rightleftharpoons \underset{\text{Weaker acid}}{H{-}NH_2} + \underset{\text{Weaker base}}{HC\equiv\overset{-}{C}\overset{+}{Na}} \quad ...(1)$$

$$\underset{\text{Stronger acid}}{H-OH} + \underset{\text{Stronger base}}{HC\equiv\overset{-}{C}\,\overset{+}{Na}} \rightleftharpoons \underset{\text{Weaker acid}}{HC\equiv CH} + \underset{\text{Weaker base}}{\overset{+}{Na}\overset{-}{OH}} \quad ...(2)$$

From (1) $HC\equiv CH$ is stronger acid than NH_3 and from (2) H_2O is stronger acid than $HC\equiv CH$. Thus we see the order of acidity is :

Acidity $H_2O > HC\equiv CH > NH_3$

How can we account for the fact that acetylene is a stronger acid than ethane ?

Here one compound X is shown to be a stronger acid than another Y by its ability to displace Y from its salt.

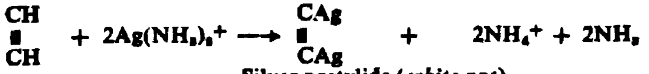
If acetylene is a stronger acid than ethane then acetylide ion ($HC\equiv C^-$) must be a weaker base than ethide ion, $C_2H_5^-$. Basicity of this ion is determined by the availability of their unshared pair of electrons for sharing with a proton.

This unshared pair in acetylide ion is in *sp* orbital while that in ethide ion is in sp^3 orbital (having more *p* character than the *sp* orbital).

An electron in a *p*-orbital is at some distance from the nucleus and is held relatively loosely. On the other hand, an electron in an *s*-orbital is close to the nucleus and is held more tightly.

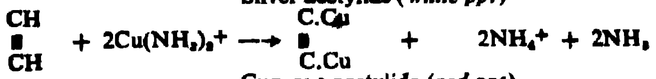
Acetylide ion is a weaker base since its unshared pair of electron is close to the nucleus and held more tightly in an sp-orbital.

(*ii*) With ammoniacal solutions of silver nitrate and cuprous chloride acetylene gives precipitates of silver acetylide (*white*) and cuprous acetylide (*red*) respectively.



$$\begin{array}{c}CH\\ \|\!|\\ CH\end{array} + 2Ag(NH_3)_2^+ \longrightarrow \begin{array}{c}CAg\\ \|\!|\\ CAg\end{array} + 2NH_4^+ + 2NH_3$$

Silver acetylide (*white ppt*)



$$\begin{array}{c}CH\\ \|\!|\\ CH\end{array} + 2Cu(NH_3)_2^+ \longrightarrow \begin{array}{c}C.Cu\\ \|\!|\\ C.Cu\end{array} + 2NH_4^+ + 2NH_3$$

Cuprous acetylide (*red ppt*)

These acetylides explode in dry state and are decomposed by mineral acids with the liberation of acetylene. This affords us a convenient method for identification of acetylene and its separation from other gases.

Mono-alkyl derivatives of acetylene (*e.g.*, $R-C\equiv CH$) give metallic derivatives (alkynides) of the formulae given below but dialkyl derivatives of acetylene (*e.g.*, $R-C\equiv C-R$) do not form such derivatives.

$R-C\equiv CNa$	$R-C\equiv CAg$	$R-C\equiv C.Cu$
Sod. alkynide	Silver alkynide	Cuprous alkynide

Acidity of 1-Alkynes. The acidic nature of hydrogen in acetylene is characteristic of hydrogen atom in the group $\equiv CH$ and is because the C—H bond has considerable ionic character due to resonance as shown below :

$$H-C\equiv C-H \longleftrightarrow H-C\equiv\overset{-}{C}\overset{+}{H} \longleftrightarrow \overset{+}{H}\overset{-}{C}\equiv CH \longleftrightarrow \overset{+}{H}\overset{-}{C}\equiv\overset{-}{C}\overset{+}{H}$$

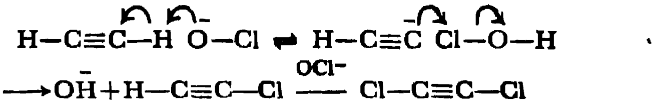
Another explanation is on the basis of electronegativity. Since π-electrons are more weakly bound than σ-electrons, the electron density round a carbon atom with π-bonds is less than that when only σ-bonds are present. In acetylene the carbon atom with two π-bonds carries a small positive charge and the hydrogen atom attached to it is released as a proton.

The acidity of 1-alkynes can also be explained in terms of the nature of the atomic orbital of the C—H bond. The *s*-character of the hybrid atomic orbital increases as we pass from sp^3 orbital (25% *s* character) to sp^2 orbital (33·3% *s* character) to *sp* orbital (50% *s* character).

The *s* character of the C—H bond is, therefore, greater in 1-alkyne formed by *sp*-*s* overlap than that in alkenes or alkanes.

Since *s* electrons are closer to the nucleus than are *p* electrons, the electrons of the C—H σ bond in 1-alkynes are closer to the nucleus and more strongly held. This facilitates the release of hydrogen atom as proton, H^+

(5) **Substitution with Halogens.** On passing acetylene into sodium hypochlorite solution at 273K in the absence of air and light, its hydrogen atoms get substituted by chlorine atoms.

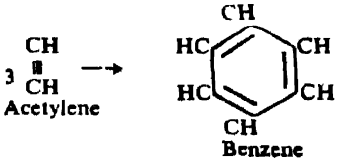


$$H—C\equiv C—H\ \ O—Cl \rightleftharpoons H—C\equiv \overset{-}{C}\ \ Cl—O—H$$
$$\longrightarrow \overset{-}{O}H + H—C\equiv C—Cl \xrightarrow{OCl^-} Cl—C\equiv C—Cl$$

Similarly diiodoacetylene is formed when acetylene is passed into a solution of iodine in liquid ammonia.

$$H—C\equiv C—H + 2I_2 + 2NH_3 \longrightarrow I—C\equiv C—I + 2NH_4I$$

(6) **Polymerisation.** When passed through a dull red hot tube, molecules of acetylene combine to give a bigger molecule, benzene, C_6H_6.



In addition to the cyclic polymerisation given above, acetylene undergoes linear polymerisation when passed into a solution of cuprous chloride in ammonium chloride to form vinylacetylene and divinylacetylene.

$$\underset{\text{Acetylene (two molecules)}}{CH\equiv CH + CH\equiv CH} \longrightarrow \underset{\text{Vinylacetylene}}{CH_2=CH—C\equiv CH}$$
$$\xrightarrow[\text{3rd molecule}]{CH\equiv CH} \underset{\text{Divinylacetylene}}{CH_2=CH—C\equiv C—CH=CH_2}$$

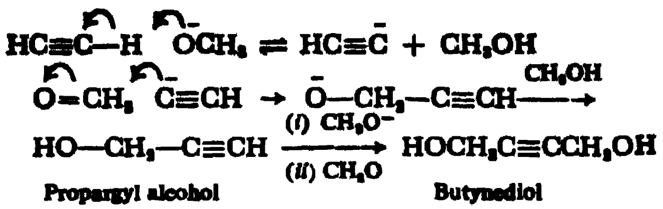
With hydrogen chloride vinylacetylene gives *chloroprene* (2-chlorobuta-1 : 3-diene) which readily polymerises to give *neoprene*, a rubber-like substance.

$$\underset{\text{Vinylacetylene}}{CH_2=CH—C\equiv CH + HCl} \longrightarrow \underset{\text{Chloroprene}}{CH_2=CH—CCl=CH_2}$$

(7) **With Nitrogen.** *When electric sparks are passed through a mixture of acetylene and nitrogen*, hydrocyanic acid is formed.

$$\underset{\text{Acetylene}}{C_2H_2} + N_2 \underset{\text{sparks}}{\overset{\text{Electric}}{\rightleftharpoons}} \underset{\text{Hydrocyanic acid}}{2H—C\equiv N}$$

(8) **With Formaldehyde.** Acetylene reacts with formaldehyde in presence of sodium alkoxide (catalyst) to give butynediol with small amount of propargyl alcohol.



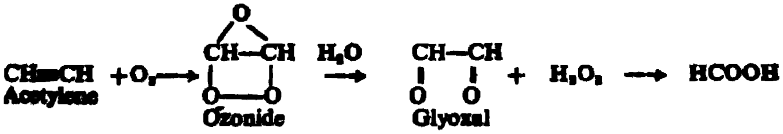
$$HC{\equiv}C{-}H \;\; \bar{O}CH_3 \rightleftharpoons HC{\equiv}\bar{C} + CH_3OH$$

$$O{=}CH_2 \;\; \bar{C}{\equiv}CH \rightarrow \bar{O}{-}CH_2{-}C{\equiv}CH \xrightarrow{CH_3OH}$$

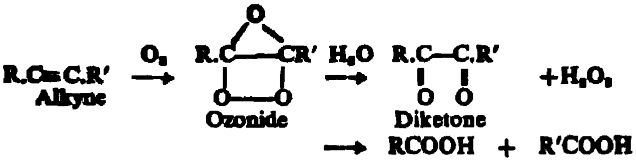
$$HO{-}CH_2{-}C{\equiv}CH \xrightarrow[(ii)\ CH_2O]{(i)\ CH_3O^-} HOCH_2C{\equiv}CCH_2OH$$

This addition of acetylene to unsaturated links like >C=O is called **ethinylation.**

(9) **With Ozone.** Acetylene gives an ozonide with ozone. The ozonide is decomposed by water to give glyoxal as well as formic acid



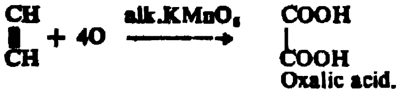
Homologues of acetylene form diketones which are further oxidised to acids.



(10) **Oxidation.** Chromic acid oxidises acetylene to acetic acid, alkaline potassium permanganate oxidises it to oxalic acid.

$$CH{\equiv}CH + H_2O + O \xrightarrow{H_2CrO_4} CH_3COOH$$

Acetic acid



$$\begin{matrix}CH\\ \|\!|\\ CH\end{matrix} + 4O \xrightarrow{alk.KMnO_4} \begin{matrix}COOH\\ |\\ COOH\end{matrix}$$

Oxalic acid.

Homologues of acetylene on oxidation with strong alkaline potassium permanganate yield mixture of acids.

$$R{-}C{\equiv}C{-}R' + H_2O + 3O \xrightarrow{alk.\ KMnO_4} RCOOH + R'COOH$$

The chain is ruptured at the position of triple bond. The nature of oxidation products can help us in locating the position of triple bond as in the case of olefins.

8. **Use of Acetylene.**— Acetylene is used : (*i*) In oxy-acetylene blowpipe for cutting and welding purposes.

(*ii*) As an illuminant.

(*iii*) For the artificial ripening of fruits.

(*iv*) In the manufacture of solvents its halogen derivatives, *eg.* $CHCl_2{-}CHCl_2$, commercially known as Westron and $CCl_2{=}CHCl$, called Westrosol.

(*v*) For the manufacture of Acetaldehyde, acetic acid, alcohol, etc.

(*vi*) In the manufacture of plastics, synthetic rubber and synthetic fibre (*orlon*).

9. Tests of Acetylene.—(*i*) It burns with a smoky flame.

(*ii*) It decolorises bromine water and alkaline permanganate solution (*Baeyer's reagent*).

(*iii*) With ammoniacal silver nitrate, it gives a white precipitate of silver acetylide.

(*iv*) With ammoniacal solution of cuprous chloride, it gives a red precipitate of curprous acetylide.

10. Structure of Acetylene.—In acetylene hybridisation of one 2*s* and one 2*p* orbital (*sp* hybridisation) is postulated in each carbon atom. Remaining two 2*p* orbitals of each carbon atom are left in their natural state.

Carbon atoms are joined to each other by an overlap of two *sp* hybrid orbitals (a sigma bond). The two C—H bonds result from *sp*-*s* overlap (these are also sigma bonds). The molecule is linear and the bond angles are 453K. The C—C distance is 1·20Å as compared with 1·34Å in ethylene and 1·54Å in ethane. The C—H distance in acetylene is 1·06Å, even shorter than in ethylene =1·086Å). This is because of their greater *s* character —*sp* orbitals are smaller than sp^2 orbitals and *sp*-hybridised carbon forms shorter bonds than sp^2-hybridised carbon.

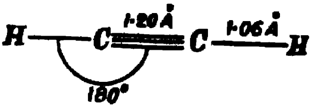


Fig. 15·4—Shape and size of acetylene molecule.

The remaining two *p*-orbitals of each carbon atom are perpendicular to one another. Sideway overlap of each *p*-orbital with a similar orbital of other carbon atoms forms two π-bonds (Fig. 15·5).

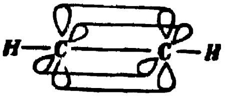


Fig. 15·5—Two pi bonds in acetylene molecule.

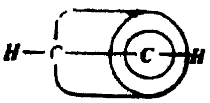


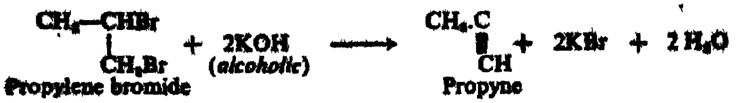
Fig. 15 6—Two pi bonds form a charge cloud having cylindrical symmetry.

This representation, however, appears to be inadeqaute. According to Coulson (1952), the two π-bonds form a charge cloud having cylindrical symmetry about the C—C axis (Fig. 15·6).

HOMOLOGUES OF ACETYLENE

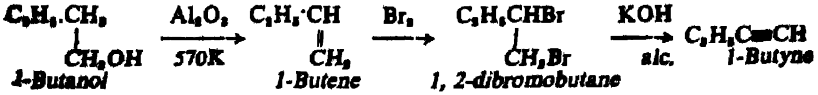
11. Preparation.—Homologues of acetylene can be prepared by the following methods :

(*i*) ***By the action of alcoholic potash on 1, 2-dihalides.***



$$\underset{\text{Propylene bromide}}{\begin{array}{l}CH_3—CHBr\\ \quad\;\; | \\ \quad\; CH_2Br\end{array}} + \underset{(alcoholic)}{2KOH} \longrightarrow \underset{\text{Propyne}}{\begin{array}{l}CH_3.C\\ \quad\;\;\, \| \! | \\ \quad\;\; CH\end{array}} + 2KBr + 2H_2O$$

This affords a convenient method for introducing a triple bond into an organic compound. For example, 1-butanol is converted into 1-butyne as follows :



$$\underset{\text{1-Butanol}}{\begin{array}{l}C_2H_5.CH_2\\ \quad | \\ \;CH_2OH\end{array}} \xrightarrow[570K]{Al_2O_3} \underset{\text{1-Butene}}{\begin{array}{l}C_2H_5\cdot CH\\ \qquad \| \\ \quad\;\; CH_2\end{array}} \xrightarrow{Br_2} \underset{\text{1, 2-dibromobutane}}{\begin{array}{l}C_2H_5CHBr\\ \qquad | \\ \quad\;\; CH_2Br\end{array}} \xrightarrow[alc.]{KOH} \underset{\text{1-Butyne}}{C_2H_5C\equiv CH}$$

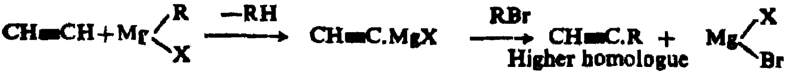
(*ii*) *By treating mono-sodium acetylide with alkyl halide.*

$$CH\equiv CH \xrightarrow[\text{Lqd. } NH_3]{\text{Na in}} \underset{\substack{\text{Mono-sodium}\\ \text{acetylide}}}{\overset{-}{CH\equiv C}.Na} \xrightarrow[-NaX]{RX} \underset{\text{Alkylacetylene}}{CH\equiv C.R}$$

These steps may be repeated to get a higher homologue (*Ascent of series*).

$$R.C\equiv CH \xrightarrow[\text{Lqd. } NH_3]{\text{Na in}} \underset{\text{Sod. alkynide}}{R.C\equiv CNa} \xrightarrow[-NaX]{R'X} \underset{\text{Dialkylacetylene}}{R.C\equiv C.R'}$$

(*iii*) *By the action of Grignard reagent on acetylene followed by reaction with an alkyl halide* (*Ascent of series*).



$$CH\equiv CH + Mg\begin{array}{l}\diagup R\\ \diagdown X\end{array} \xrightarrow{-RH} CH\equiv C.MgX \xrightarrow{RBr} \underset{\text{Higher homologue}}{CH\equiv C.R} + Mg\begin{array}{l}\diagup X\\ \diagdown Br\end{array}$$

12. **Properties.**—The properties of the homologues of acetylene are very similar to those of acetylene especially when these are of the type $R.C\equiv CH$. The common properties are in fact properties of the $\equiv CH$ group.

An interesting property of the homologues which has not been discussed under acetylene is their **ability to isomerise** as explained below :

(*i*) *On heating with alcoholic potash* the isomerisation occurs due to shifting of the triple bond towards the centre. For example,

$$\underset{\text{1-Butyne}}{CH_3.CH_2C\equiv CH} \xrightarrow[\text{heat}]{+\text{alc. KOH}} \underset{\text{2-Butyne}}{CH_3\,C\equiv C.CH_3}$$

(*ii*) *On heating with sodamide in an inert solvent* the triple bond moves towards the end. For example,

$$\underset{\text{2-Butyne}}{CH_3C\equiv C.CH_3} \xrightarrow[-NH_3]{NaNH_2} \underset{\text{Sod. alkynide}}{CH_3\,CH_2C\equiv CNa} \xrightarrow{H_2O} \underset{\text{1-Butyne}}{CH_3.CH_2.C\equiv CH}$$

13. **Diacetylenes.**—Compounds having a pair of triple bonds are called **diacetylenes** (*cf.* diolefins). Two important members of the class are :

$$\underset{\text{Diacetylene}}{HC\equiv C-C\equiv CH}\,; \qquad \underset{\text{Dipropargyl}}{CH\equiv C.CH_2.CH_2.C\equiv CH}$$

Dipropargyl is prepared by bromination of 1,5-hexadiene followed by treatment with alcoholic potash.

It is isomeric with benzene. It is a liquid (b.p. 358K) lighter than water (sp. gr. 0·81). Chemically it behaves like acetylene.

The monovalent group $HC\equiv C—CH_2—$ is called propargyl or propinyl.

14. Ascent and Descent of Series and Typical Conversions.—

(*a*) *Conversion of Paraffin into Olefin or Acetylene.* A double bond is introduced by dehydration of alcohol or treating an alkyl halide (*except ethyl halide*) with alcoholic potash. A double bond may be replaced by a triple bond by adding bromine and treating the dibromide obtained with alcoholic potash. For example,

$$\underset{\text{Ethane}}{CH_3—CH_3} \xrightarrow[h\nu]{Cl_2} \underset{\text{Ethyl chloride}}{CH_3—CH_2Cl} \xrightarrow[\text{aq.}]{KOH} \underset{\text{Ethanol}}{CH_3—CH_2OH} \xrightarrow[420\text{-}430K]{H_2SO_4} \underset{\text{Ethylene}}{CH_2=CH_2}$$

$$\underset{\text{Propane}}{CH_3.CH_2.CH_3} \xrightarrow[h\nu]{Cl_2} \underset{\text{Isopropyl chloride}}{CH_3.CHCl.CH_3} \xrightarrow{KOH,\ \text{alc.}} \underset{\text{Propylene}}{CH_3.CH=CH_2}$$

$$\underset{\text{Ethylene}}{CH_2=CH_2} \xrightarrow{Br_2} \underset{\text{Ethylene bromide}}{CH_2Br—CH_2Br} \xrightarrow{KOH\ \text{alc.}} \underset{\text{Acetylene}}{CH\equiv CH}$$

(*b*) *Ascent and Descent of series in Olefins.* For example, ethylene is converted into propylene and *vice versa* as follows :

$$\underset{\text{Ethylene}}{CH_2=CH_2} \xrightarrow{HI} \underset{\text{Ethyl iodide}}{CH_3CH_2I} \xrightarrow[\text{in dry ether}]{CH_3I+Na} \underset{\text{Propane}}{CH_3.CH_2CH_3} \xrightarrow{Cl_2}$$

$$\underset{\text{Isopropyl chloride}}{CH_3.CHCl.CH_3} \xrightarrow{KOH\ \text{alc.}} \underset{\text{Propylene}}{CH_3.CH=CH_2} \xrightarrow{Ozonolysis}$$

$$\underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{H} \underset{\text{Ethanol}}{CH_3.CH_2OH} \xrightarrow[420\text{-}430K]{H_2SO_4} \underset{\text{Ethylene}}{CH_2=CH_2}$$

(*c*) *Ascent and Descent of series in Alkynes.* For example, conversion of ethyne into propyne and *vice versa.*

$$\underset{\text{Ethyne}}{CH\equiv CH} \xrightarrow[\text{Lqd.}NH_3]{\text{Na in}} \underset{\text{Sod. acetylide}}{CH\equiv CNa} \xrightarrow{CH_3I} \underset{\text{Propyne}}{CH\equiv C.CH_3}$$

$$\xrightarrow{H_2} \underset{\text{Propane}}{CH_3CH_2CH_3} \xrightarrow[\text{in }(b)\text{ above}]{\text{By steps given}} \underset{\text{Ethylene}}{CH_2=CH_2}$$

$$\xrightarrow{Br_2/CCl_4} \underset{\text{Ethylene bromide}}{CH_2Br—CH_2Br} \xrightarrow[\text{alc.}]{KOH} \underset{\text{Acetylene}}{CH\equiv CH}$$

QUESTIONS

A. Essay Type :

1. What organic substance is produced when water acts on calcium carbide ? Write an account of its purification and collection. How does it react with (*a*) HI, (*b*) H_2SO_4, (*c*) O_3, and (*d*) ammoniacal CuCl ?

(*Delhi B.Sc. Hons. Sub. 1977 Supp.*)

2. What are the general methods of preparation of acetylene compounds and what are their usual properties ? What explanation would you offer for their great instability ? Describe the synthetic and industrial use of acetylene.

3. (*a*) How is acetylene prepared ? Describe its chief properties and uses.

(*b*) Explain why the hydrogen atoms in acetylene are replaceable by metals. (*Delhi B.Sc. Hons. Part I 1973*)

4. (*a*) Discuss the important methods for the preparation of acetylene.

(*b*) Starting from acetylene how will you obtain each of the following compounds ?

(*i*) Acetaldehyde (*ii*) Ethyne (*iii*) Vinyl chloride. (*Osmania B.Sc. 1979*)

5. Compare the properties of ethylene and acetylene. Write a note on the industrial importance of acetylene.

6. Complete the following reactions (write all equations in full) :

(*a*) 2-Pentyne and $KMnO_4$. (*b*) 2-Butyne+Ozone followed by hydrolysis. (*c*) Ethylidene acetate when heated. (*d*) Vinylacetylene+hydrochloric acid.

7. How will you effect the following conversions ?

(*a*) Propane into propyne and *vice versa*. (*b*) Acetylene into propane and *vice versa*. (*c*) 1-Butanol into 1-Butyne. (*d*) 1-Butyne into 2-Butyne and *vice versa*. (*e*) Acetylene into Lewisite. (*f*) Acetylene into chloroprene. (*g*) 1, 5-Hexadiene into dipropargyl.

8. Discuss the structure of acetylene on the basis of orbital theory. Explain with examples why acetylene shows acidic, electrophilic addition and nucleophilic addition reactions. (*G.N.D. B.Sc. 1975*)

B. Short-Answer Type :

1. Why are hydrogen atoms in acetylene more acidic than those in ethylene ? (*Delhi B.Sc. Hons. 1977*)

2. Explain why acetylene is acidic in nature. (*Delhi B.Sc. 1977*)

3. How is the following pair distinguished ? Give one reaction.

$CH_3.CH_2.C\equiv CH$ and $CH_3.C\equiv C.CH_3$

(*Delhi B.Sc. Hons. Sub. 1977*)

4. What happens when acetylene is passed through warm acetic acid in the presence of mercuric ions ? (*Delhi B.Sc. Hons. 1977*)

5. Write and draw an orbital structure of acetylene,

(*Guru Nanak Dev B.Sc. 1977*)

6. Give two properties each of electrophilic and nucleophilic additions on acetylene along with their mechanisms. (*Guru Nanak Dev B Sc. 1977*)

7. Account for the fact—Acetylene forms a sodium derivative but ethylene does not. (*Madras B.Sc. 1976 September*)

8. Give the shapes and bond angles of (*i*) ethylene and (*ii*) acetylene. Mention the state of hybridisation of carbon in these compounds.

(*Osmania B. Sc. 1975*)

9. How are alkynes distinguished from alkenes. (*Marathwada B.Sc. 1976*)

10. Write a short note on Markownikoff's rule.

(*Marathwada B.Sc. 1976 ; Madras 1976*)

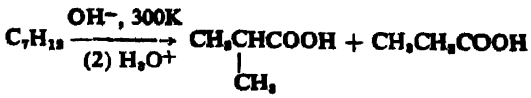
11. Write the structural formulae for :

(*a*) 2-4-Methylpentyne ; (*b*) Diethylacetylene ;
(*c*) Dimethylacetylene ; (*d*) 3, 4, 4-Trimethyl-1-pentyne.

Give IUPAC names of (*b*) and (*c*).

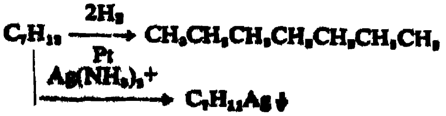
Which of these compounds give a positive test with $Ag(NH_3)_2^+OH^-$?

12. Give the name and structure of each of the following alkynes :

(*a*)


$$C_7H_{12} \xrightarrow[\text{(2) } H_3O^+]{\text{(1) } KMnO_4,\ OH^-,\ 300K} \underset{\underset{CH_3}{|}}{CH_3CHCOOH} + CH_3CH_2COOH$$

$$\text{(b)}\quad C_8H_{12} \xrightarrow[\text{(2) } H_3O^+]{\text{(1) } KMnO_4,\ OH^-,\ 300K} HOOC\text{—}(CH_2)_6\text{—}COOH \text{ (only)}$$

(*c*)


$$C_7H_{12} \xrightarrow[Pt]{2H_2} CH_3CH_2CH_2CH_2CH_2CH_2CH_3$$

$$C_7H_{12} \xrightarrow{Ag(NH_3)_2^+} C_7H_{11}Ag\downarrow$$

13. Give the structure of the products obtained when 1-pentyne reacts with :

(*a*) one mole of Br_2 (*b*) one mole of HCl

(*c*) two moles of HCl (*d*) one mole of HBr and a peroxide

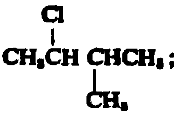
(*e*) H_2O, H^+, Hg^{2+}, (*f*) H_2, Pd-$CaCO_3$, quinoline

(*g*) $NaNH_2$ in liq. NH_3 and then with C_2H_5I,

(*h*) $Ag(NH_3)_2OH$, (*i*) Hot $KMnO_4$.

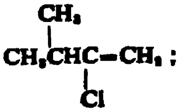
14. Starting with 3-methyl-1-butene, how can the following compounds be synthesised :

(*a*)



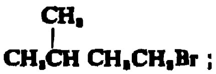
$CH_3\underset{}{\overset{Cl}{\overset{|}{C}H}}\ \underset{\underset{CH_3}{|}}{C}HCH_3$;

(*b*)



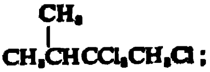
$CH_3\overset{CH_3}{\overset{|}{C}H}\underset{\underset{Cl}{|}}{C}{-}CH_3$;

(*c*)



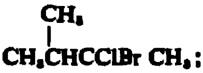
$CH_3\overset{CH_3}{\overset{|}{C}H}\ CH_2CH_2Br$;

(*d*)



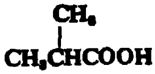
$CH_3\overset{CH_3}{\overset{|}{C}H}CCl_2CH_2Cl$;

(*e*)



$CH_3\overset{CH_3}{\overset{|}{C}H}CClBr\ CH_3$;

(*f*)



$CH_3\overset{CH_3}{\overset{|}{C}H}COOH$

15. Explain why $CH_3C{\equiv}CH$ has only one acidic hydrogen.
(*Aligarh B.Sc. 1979 Supp.*)

C. Problems :

1. An organic compound A with molecular formula C_5H_8 forms a sodio-derivative which reacts with C_3H_7I (B) to give a compound C_8H_{14} (C) which gives *n*-octane on further reduction. Identify the compounds A, B and C. Write chemical equations for the various reactions involved.

2. An alkyne A with molecular formula C_5H_8 reacts neither with sodamide nor with ammoniacal cuprous chloride. Assign a structural formula to A.

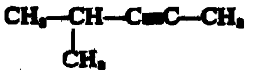
3. An organic compound A with molecular formula C_6H_{10} when treated with sodium in liquid ammonia followed by treatment with *n*-propyl iodide yields C_9H_{16} (B). When treated with dilute sulphuric acid containing mercuric sulphate, A gives the ketone $C_6H_{12}O$ (C). On oxidation with alkaline potassium permanganate B gives two isomeric acids $C_4H_8O_2$ (D and E). Identify the compounds A to E.

4. With alcoholic potash $C_5H_8Cl_2$ (A) gives C_5H_8 (B) which reacts with ammoniacal cuprous chloride. Identify the compounds A and B.

5. Three compounds A, B and C are isomers of the formula C_5H_8. All of them decolorise bromine in CCl_4 and give a positive test with Baeyer's reagent. All the three dissolve in conc. H_2SO_4. Compound A gives a white ppt with ammoniacal silver nitrate whereas B and C do not react with it. On hydrogenation in presence of platinum catalyst, A and B both yield *n*-pentane whereas C gives a product of formula C_5H_{10}. On oxidation with hot acidified $KMnO_4$ B gave acetic acid and CH_3CH_2COOH. Identify A, B and C.

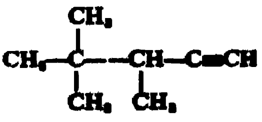
ANSWERS

B. 11. (*a*)



$CH_3{-}\underset{\underset{CH_3}{|}}{C}H{-}C{\equiv}C{-}CH_3$

(*d*)



$CH_3{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}\underset{\underset{CH_3}{|}}{C}H{-}C{\equiv}CH$

(*b*) $C_2H_5{-}C{\equiv}C{-}C_2H_5$

(*c*) $CH_3{-}C{\equiv}C{-}CH_3$.

IUPAC names :

(*b*) 3-Hexyne ; (*c*) 2-Butyne.

C. 1. A is $CH_3.CH_2.CH_2C{\equiv}CH$ (1-Pentyne).
B is $CH_3.CH_2.CH_2I$ (*n*-propyl iodide).
C is $CH_3.CH_2.CH_2C{\equiv}C.CH_2CH_2.CH_3$ (4-Octyne).

2. $CH_3C{\equiv}C.CH_2.CH_3$ (2-Pentyne)

3. A is $(CH_3)_2CH.C{\equiv}CH$ (3-Methyl-1-butyne)
B is $(CH_3)_2CH.C{\equiv}C.CH_2.CH_2.CH_3$ (2-Methyl-3-heptyne)
C is $(CH_3)_2CH.CO.CH_3$ (3-Methylbutanone).
D is $(CH_3)_2CH.COOH$ (isobutyric acid).
E is $CH_3.CH_2.CH_2.COOH$ (butyric acid).

4. A is $C_2H_5.CH_2.CHCl_2$. or $C_2H_5.CHCl.CH_2Cl$
1, 1-dichlorobutane *1, 2-dichlorobutane*
B is $C_2H_5{-}C{\equiv}CH$ *(1-butyne).*

5. A is $CH_3CH_2CH_2C \equiv CH$ (1-pentyne)
B is $CH_3CH_2C \equiv CCH_3$ (2-pentyne)
C is cyclopantene.

16

Petroleum

1. **What is Petroleum** ?—With the advance of civilisation the means of communication have been revolutionised. A journey which took months in the past is now completed in a few days in buses and cars. The same journey does not take more than a few hours if you travel by an aeroplane. All these vehicles run on petrol. Petrol is a refined product obtained from a naturally occurring crude oil called petroleum.

2. **Occurrence of Petroleum**.—As usually obtained, petroleum or crude oil is a viscous, dark coloured (varying from amber to black), fluorescent oil and often has a definite offensive odour. It is generally trapped deep below layers of earth and often floats on salt water. The oil is covered by an atmosphere of the more volatile hydrocarbons, the *natural gas*—which consists chiefly of the first six paraffins.

The biggest oil-producing country of the world is the United States of America. Others in the order of the total production are : Russia, Venezuela, Iran, Mexico, Rumania, Iraq, Burma, India and Pakistan.

Petroleum Resources of India. Our oil-fields are located in Assam and Gujarat.

In Gujarat the oil-fields are located at Cambay and Ankleshwar. Another oil-field of substantial size has been discovered near Kalol, 25 kilometres north of Ahmedabad and 125 km from Cambay, and is likely to be the richest oil-field in India.

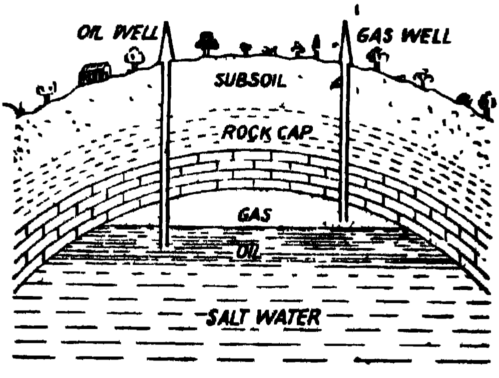


Fig. 16·1—Occurrence of Petroleum or Crude oil.

In 1978 ONGC discovered gas at Sisodra, Gajera, West Matwan and Walner in Gujarat and oil toghther with gas at Viraj and West Sobhasan in Gujarat. In 1978-79 sub-sea pipeline from Bombay High to Uran and transfer line from Uran to Trombay was completed. Oil and gas started flowing through these in July 1978. Rate of production is about 44 lakh tonnes per annum.

By the end of June, 1979 total number of wells drilled in the onshore area was 1548 and of these 842 were found to be oil bearing and 103 gas bearing Number of wells drilled in the offshore area was 104 and out of these 59 were oil bearing and 11 gas bearing.

Various refineries working in the country with their refining capacity and actual production are given on the next page I

Name of refinery	*Year in which production started*	*Capacity (in lakh tonnes) 1.4.79*	*Actual crude run (lakh tonnes)*	
			1977-78	*1978-79*
Barauni (IOC)	1964	33·0	30·6	26·61
BPCL, Bombay	1955	52·5	42·12	46·93
BR & PL	1979	10·0	—	0·57
Cochin	1966	33·0	29·33	28·62
Digboi	1901	5·0	5·34	5·24
Gauhati (IOC)	1962	8·5	8·17	8·25
Haldia	1975	25·0	20·96	22·13
HPCL, Bombay	1954	35·0	28 97	28·00
HPCL, Vishakhapatnam	1957	15·0	13·04	13·39
Koyali (IOC)	1965	73·0	41·29	52·56
Madras	1969	28·0	26·16	27·59

Excepting the 5-lakh tonne Digboi refinery and the Assam Oil Company, the rest are in the public sector.

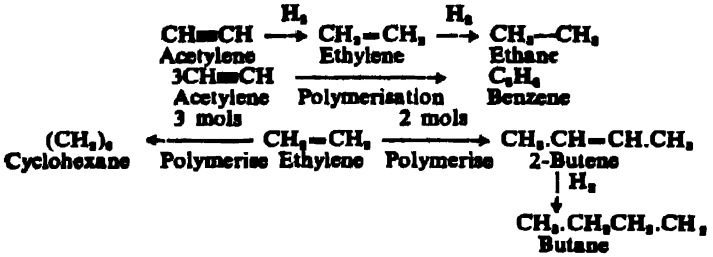
The 1 million tonne Bongaigaon refinery and the adjacent petrochemicals complex in Assam has recently been completed and crude distillation unit went on stream in February, 1979. The 6 million tonne Mathura refinery has since gone on stream.

3. **Composition of Petroleum.**—The composition of crude oil varies with places of occurrence but all contain alkanes (from C_1 to C_{40}), cycloalkanes or naphthenes and aromatic hydrocarbons. The low-boiling fractions of petroleum, irrespective of its locality of occurrence, are composed of alkanes. The composition of higher boiling fractions, however, differs according to the source. Besides hydrocarbons, there are also present certain organic compounds containing oxygen, nitrogen and sulphur.

If the residue obtained after removal of volatile compounds of crude oil is rich in paraffins or wax, the petroleum is termed *paraffinic*. On the other hand, if the residue is rich in naphthenes, (*cycloparaffins*), it is classified as asphaltic. Crude oil from Pennsylvania, Iran, Iraq and Rumania has been found to be paraffinic and that obtained from Baku and Venezuela asphaltic. Crude oil from Texas and Mexico has been found to be both paraffinic and asphaltic.

4. **Origin of Petroleum in Nature.**—The origin of petroleum and natural gas is still uncertain. Many theories have been suggested to explain the formation of petroleum in nature. For example,

(*a*) **Carbide Theory.** Mendeleeff suggested that petroleum has been produced inside the earth by the action of water on metallic carbides (*inorganic origin*). It was later on supported by Moissan, Sabatier and Senderens. Lower unsaturated hydrocarbons first produced (*e.g.*, acetylene by the action of water on calcium carbide) undergo hydrogenation and polymerisation to give alkanes, cycloalkanes and aromatic hydrocarbons.



$$\underset{\text{Acetylene}}{CH\equiv CH} \xrightarrow{H_2} \underset{\text{Ethylene}}{CH_2=CH_2} \xrightarrow{H_2} \underset{\text{Ethane}}{CH_3-CH_3}$$

$$\underset{\text{Acetylene}}{3CH\equiv CH} \xrightarrow[\text{Polymerisation}]{} \underset{\text{Benzene}}{C_6H_6}$$

$$\underset{\text{Cyclohexane}}{(CH_2)_6} \xleftarrow[\text{Polymerise}]{\text{3 mols}} \underset{\text{Ethylene}}{CH_2=CH_2} \xrightarrow[\text{Polymerise}]{\text{2 mols}} \underset{\text{2-Butene}}{CH_3.CH=CH.CH_3} \xrightarrow{H_2} \underset{\text{Butane}}{CH_3.CH_2CH_2.CH_3}$$

and so on.

Moissan actually got a petroleum-like liquid by the action of water on uranium carbide. The theory, however, fails to explain the following facts about petroleum :

(*i*) It is optically active. (*ii*) It is found to contain certain sulphur and nitrogen compounds.

(*b*) **Engler's Theory.** Engler proposed in 1900 that petroleum is produced by the decomposition of marine animals under high pressure and temperature (*Animal origin*). By heating fish-oil and certain animal fats under pressure, he actually produced a liquid resembling petroleum. Various points in favour of the theory are :

(*i*) Petroleum is optically active and contains sulphur and nitrogen compounds. This suggests organic origin of petroleum.

(*ii*) Its association with brine suggests its origin in sea.

(*iii*) Fossils have been discovered in the petroleum areas. These are the remains of the marine animals which died long, long ago.

(*c*) **Modern Theory.** Engler's theory fails to explain the presence of certain chlorophyll derivatives in many oils. This points to the *vegetable origin* of petroleum. High resin content of certain oils (*e.g.*, Burma oil) is also accounted for by the vegetable origin of petroleum.

Petroleum is now believed to be a material resulting from the partial decomposition of marine animals and vegetable organisms in pre-historic forests. Changes in earth's crust have buried this material underground where it has been subjected to intense pressure during the ages. The conversion of organic matter into petroleum has been going on—

(*a*) *either under the influence of radioactive substances such as uranium*,

(*b*) *or by bacterial decomposition under pressure.*

This seems to be the most plausible explanation and facts in support of it are :

(*i*) Association of petroleum with brine (originally sea-water) and presence of coal deposits (originating from pre-historic forests) usually present in their neighbourhood indicate towards its animal and vegetable origin.

(*ii*) Distillation of animal fats and fish-oil under pressure yields a liquid closely resembling petroleum.

(*iii*) Optical activity of petroleum and the presence of nitrogen and sulphur compounds derived from haemin (pigment of blood) and chlorophyll along with the presence of resins in some oils also point to its vegetable or animal origin.

5. **Mining of Petroleum.**—Petroleum occurs at different depths varying from a few hundred metres to about 3 km. It is extracted by drilling holes in the earth's crust and sinking pipes until *the drill penetrates the oil-bearing sands. Sometimes the oil rushes out through them due to the pressure exerted by the natural gas inside.*

As the pressure of the gas diminishes, the oil is obtained by pumping. Pumping is done by ordinary lift pumps. Recently so-called air-lift has become more common. Two coaxial pipes are lowered into the bore and compressed air is forced down through one pipe. As this rises up through the other pipe it carries a froth of oil similar to the oil, natural gas mixture which comes out in the beginning. From the oil-fields the crude oil is taken to refineries through pipelines about 20 cm in diameter laid on the ground or buried a few metres underground.

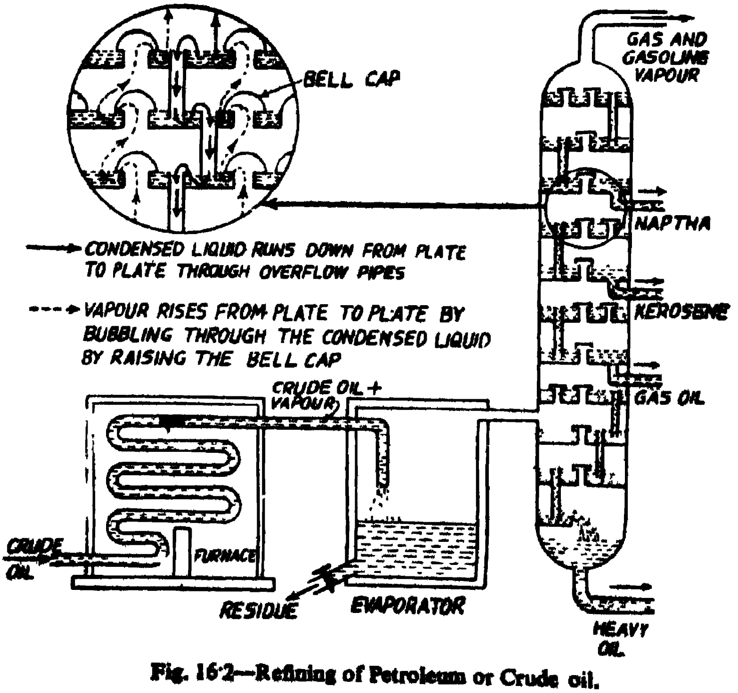

BELL CAP
GAS AND GASOLINE VAPOUR
NAPTHA
KEROSENE
GAS OIL
HEAVY OIL
CONDENSED LIQUID RUNS DOWN FROM PLATE TO PLATE THROUGH OVERFLOW PIPES
VAPOUR RISES FROM PLATE TO PLATE BY BUBBLING THROUGH THE CONDENSED LIQUID BY RAISING THE BELL CAP
CRUDE OIL + VAPOUR
CRUDE OIL
FURNACE
RESIDUE
EVAPORATOR

Fig. 16·2—Refining of Petroleum or Crude oil.

Refineries are always located at a distance of a few miles from the oil-field. This is because these are to be located at points well-connected with the consuming centres, so that the cost of transport of refined products to the market is minimum. These are connected with the oil-fields by means of a pipe-line. The crude oil flows through the pipe-line and thus involves no expenditure.

6. **Refining of Crude Oil.**—Crude oil is a mixture of dissolved *gases, liquids,* with low, medium and high boiling points and of widely varying viscosities and *solids and semi-solids.* Refining is the process of separation of this mixture by fractional distillation into more useful and, therefore, more valuable products.

In most modern refineries, petroleum is refined by continuous distillation in pipe stills and saves time, labour and fuel. The essentials of a pipe-still installation are :

(*i*) Dark-coloured, fluorescent emulsion of sandy oil and water—crude petroleum, is warmed under pressure with steam coils in iron tanks with conical bases. This breaks the emulsion into two layers. The gas, oil and solids are drawn off separately. *The gases evolved are mainly used as fuel but a portion is liquefied*

(*ii*) The upper layer of crude oil, thus removed, is used as cooling agent in the condensers, where it gets heated to about 420 K.

(*iii*) This oil at about 420 K is passed through several hundred metres long coil of pipes, heated in a fire box. Here it gets heated to about 670K.

(*iv*) The heated crude oil then enters a large insulated vessel called the *evaporator.* No external heat is applied to the evaporator. All components, volatilizing up to 670 K, vaporise and escape at the top leaving a residue of the fuel oil which is periodically removed from the bottom of the evaporator.

(*v*) The vapours from the evaporator are passed up a *fractionating column.* Here *fractional condensation* occurs.

Let us understand how the fractional condensation is taking place in the fractionating column. The upgoing hot vapours cool and condense on the plates. Condensed liquid runs down from plate to plate through overflow pipes. The upgoing hot vapours raise the bell cap and bubble through the condensed liquid.

The liquid gets heated a little and loses the more volatile constituent by evaporation. At the same time hot vapours are cooled and lose less volatile component by condensation. Thus more volatile components keep on rising up in the form of vapours and less volatile components keep on travelling downwards as liquid.

Hence the high-boiling fractions condense in the lower part of the column and the low-boiling fractions in the upper part of the column. These fractions are refractionated and purified to get various products.

7. **Products obtained and their Uses.**—In the table given on the next page are listed the fractions usually separated with their boiling ranges and uses.

Fractions	Boiling Range (K)	Uses
1. **Gas**	Below room temp.	Fuel, manufacture of gasoline (by polymerisation) and rubber.
2. **Crude Naphtha** *On refractionation further gives*	290-420	
(*a*) Petroleum ether	290-340	As solvent in varnish and rubber industries ; for dry-cleaning.
(*b*) Petrol or gasoline	340-360	Motor fuel ; *dry-cleaning ; for making petrol air gas.*
(*c*) *Ligroin* or light petroleum	360-390	As solvent , in dry-cleaning.
(*d*) Benzine	390-420	In varnish ; in dry-cleaning.
3 **Kerosene**	420-470	As fuel and illuminant ; for making oil gas
4. **Gas oil or Heavy oil**	Above 570	As fuel in diesel engines ; cracked to yield more gasoline.
5. **Residue from Evaporator** *On fractionation by vacuum distillation is separated into*	Above 670	
(*i*) *Paraffin wax*	On cooling	For making candles and boot polishes.
(*ii*) *Lubricating oils*		For lubrication
(*iii*) *Vaseline*		In toilet goods, ointments and for lubrication
(*iv*) *Pitch*		In paints and varnishes ; tarring roads.
(*v*) *Petroleum coke*	On redistilling tar	As fuel.

8. Further Refining of Gasoline.—Refining of gasoline is necessary to remove its objectionable colour, odour and sulphur compounds which lower its response to anti-knock compounds.

'Sour' gasoline (as it is commonly called) is washed with concentrated sulphuric acid or sodium hyrdoxide to remove thioalcohols. Washing is followed by sweetening (addition of alkaline sodium plumbite), if necessary. Sodium plumbite oxidises thioalcohols to disulphides.

$$\underset{\text{Thioalcohol}}{2RSH} + \underset{\substack{\text{Sodium}\\ \text{plumbite}}}{Na_2PbO_2} + \underset{\substack{\text{Calculated}\\ \text{amount}}}{S} \longrightarrow \underset{\text{Disulphide}}{R{-}S{-}S{-}R} + PbS + 2NaOH$$

9. How do Refiners increase the yield of Gasoline ?—Crude petroleum contains only a small percentage of the low boiling fraction, gasoline. The refiners increase the yield of gasoline by a number of methods, such as the following :

(*a*) **By Cracking.** Cracking has been simply defined as "making of little molecules out of big ones". This is done by heating the high boiling fraction when the bigger molecules break up into smaller ones of much lower boiling points. Thus cheap heavy oils which are much less in demand are converted into petrol. About 50 per cent of our gasoline is now obtained by this method.

There are two main types of cracking : (*i*) liquid phase, and (*ii*) vapour phase.

(*i*) **Liquid phase cracking.** Heavy oil is cracked by heating at a suitable temperature (750-800 K) under 7 to 68 atmospheres pressure. High pressure is necessary to maintain the cracked material *in liquid state. The yield of gasoline is about 60-65 per cent.*

(*ii*) **Vapour phase cracking.** Kerosene or any other oil with similar boiling range is heated to 870 K under 3·5 to 10 atmospheres pressure. Heavy oils cannot be cracked by this method since these cannot be completely vaporised under these conditions.

(*b*) **By Polymerisation.** In polymerisation simple hydrocarbons such as C_2H_4, etc., are polymerised or bunched to give molecules of the proper size of gasoline. The process is thus the opposite of cracking and is carried out by heating the hydrocarbons with a suitable catalyst like phosphoric acid.

Large amounts of unsaturated hydrocarbons are formed during cracking. These are polymerised into liquid gasoline and used as motor fuel.

10. Synthetic Gasoline.—With the advance of civilization, the consumption of gasoline has increased much and the demand is still on the increase. In spite of the marvellous achievements of the oil chemists in the direction of increasing the proportions of gasoline obtained from crude oil, it is feared that the world's supplies of natural petroleum might be exhausted before long. This fear has made the modern chemist turn to what may be termed "*synthetic gasolines*, *i.e.*, those which do not have their origin in crude oil. Among proved methods of manufacture, the two most promising are :

(*i*) **Bergius Process.*** Coal is largely a mixture of solid hydrocarbons and may be hydrogenated to produce low boiling hydrocarbons. This is Bergius process for the manufacture of synthetic petroleum. Coal dust is made into a paste with heavy oil or coal-tar and then a catalyst composed of organic compound of tin is incorporated. The whole is heated to 670-870K under 200-250 atmosphere pressure in the presence of hydrogen. Hydrogenation of coal takes place and a product resembling crude oil is obtained.

Crude oil is subjected to fractional distillation when the following fractions are obtained :

(*i*) Gasoline, (*ii*) Middle oil, and (*iii*) Heavy oil.

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* Friedrich Bergius (1884-1940)—German chemist, after his name we have the Bergius process for the manufacture of synthetic gasoline. Another of his processes was the hydrolysis of wood to sugar and cattle feed. He was awarded Nobel Prize for chemistry in 1938.

The middle oil is hydrogenated in the vapour phase in presence of a solid catalyst when it gives gasoline. Heavy oil is again used for making a paste with coal dust. The yield of gasoline by Bergius process may be as high as 60 per cent (on the basis of coal dust used).

In India we have a limited number of oil-fields but there are vast coal-fields. We can, therefore, count upon our coal-fields to supply synthetic petrol. Efforts are being made to set up a plant for the manufacture of synthetic petrol by Bergius process. A 1,00,000-tonne capacity plant will cost about twenty crores of rupees.

(ii) **Fischer-Tropsch Process.** Steam is blown over red hot coke to get water gas ($CO+H_2$). Water gas mixed with half its volume of hydrogen is then passed over the catalyst at 470-870K under 1-10 atm pressure.

$$xCO + yH_2 \rightarrow \underset{\textit{(Saturated and unsaturated)}}{\text{Mixture of hydrocarbons}} + H_2O$$

Various metals and oxides have been used as catalyst. One of the best known catalysts is a mixture of cobalt (100 parts), thoria (5 parts), magnesia (8 parts) and kieselguhr (200 parts). When the pressure maintained is 9-10 atmospheres, more of high boiling fraction is obtained. To get more gasoline reaction is carried out under atmospheric pressure.

The crude oil obtained is refined by fractional distillation as in the case of petroleum. The high boiling fractions are cracked to get more gasoline.

11. Knocking and Octane Rating.—In an internal combustion engine the fuel mixture of gasoline vapour and air burns within the working cylinder. Mixture is fired by means of a spark from the sparking plug. For maximum efficiency the fuel mixture must be highly compressed before firing in the cylinder. The modern automobile engines squeeze this mixture to one-seventh or even to one-eighth of its normal volume.

As the compression ratio increases, a point is reached when the *knocking* is observed. On sparking all the fuel does not burn smoothly, the end portion burns with explosive violence giving rise to a metallic rattle called knocking. This results in the loss of power.

It has, however, been found that tendency to knock falls off with change in the nature of the fuel as follows :

Straight-chain paraffins > branched-chain paraffins > olefins > naphthenes > aromatics.

Octane rating of a gasoline is a number. It is a convenient device for rating the anti-knock qualities of a gasoline. The higher the number, the lesser the tendency of the gasoline to knock in a high compression engine.

Edgar introduced (in 1927) 2, 2, 4-trimethylpentane (incorrectly known as isooctane) which has excellent anti-knock properties and *n*-heptane which knocks far more badly than commercial gasoline as *standards for rating the anti-knock properties of a fuel. Isooctane is given an arbitrary rating of 100 while normal heptane is given a rating of zero.* All other fuels are compared with their mixture in suitable proportions.

Octane rating or Octane number of gasoline is the percentage of isooctane in the mixture of isooctane and n-heptane which matches the fuel in knocking. Suppose the gasoline being tested behaves like a mixture of 70% isooctane and 30% *n*-heptane, its octane number is 70. Good gasolines have a rating of 90 or higher. Aviation gasoline (gasoline used in aeroplanes) has a rating of 100. Gasoline with rating higher than 100 have been produced.

Prevention of knocking. Methods employed for preventing or minimising knocking are :

(1) **By adding antiknock compounds.** Tetraethyllead (TEL) is one such compound which when added to gasoline minimises knocking. It moderates the combustion of gasoline so that it burns smoothly. This, however, leads to the deposition of lead metal in the engine. Ethylene bromide is mixed with leaded gasoline to prevent this deposition of lead. The metal is converted into lead bromide (a volatile product) which escapes with exhausted gases.

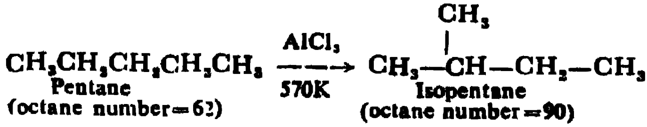
$$\underset{\text{Ethylene bromide}}{Pb + CH_2Br{-}CH_2Br} \longrightarrow \underset{(\textit{volatile})}{PbBr_2} + CH_2{=}CH_2$$

(2) **Other methods.** Lead being toxic, lead bromide escaping from the exhaust pipe is a dangerous pollutant of atmosphere. The modern trend is, therefore, to improve octane number without adding TEL. It has been found that tendency to knock falls off with change in the nature of hydrocarbons in the fuel as follows :

Straight-chain paraffins > branched-chain paraffins > olefins > napthenes > aromatic hydrocarbons.

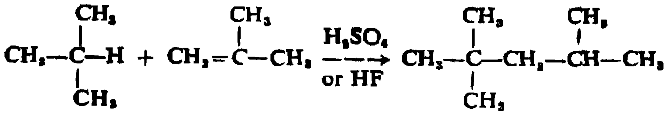
Octane number of a fuel can be improved by enhancing the percentage of branched-chain alkenes and aromatic hydrocarbons in the gasoline. Some of the methods used for getting no-lead gasoline with improved octane number are :

(*i*) **Isomerisation** (*also termed* **Reforming**). By passing gasoline vapours over $AlCl_3$ (catalyst) at 570K.



$$\underset{\substack{\text{Pentane}\\ \text{(octane number}=62)}}{CH_3CH_2CH_2CH_2CH_3} \xrightarrow[570K]{AlCl_3} \underset{\substack{\text{Isopentane}\\ \text{(octane number}=90)}}{CH_3{-}\overset{\overset{\displaystyle CH_3}{|}}{C}H{-}CH_2{-}CH_3}$$

(*ii*) **Alkylation.** Cracking of petroleum is accompanied by alkylation too. For example, isobutylene produced during cracking alkylates isobutane to form isooctane.



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-H + CH_2=\overset{CH_3}{C}-CH_3 \xrightarrow[\text{or HF}]{H_2SO_4} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\overset{CH_3}{CH}-CH_3$$

2, 2, 4-Trimethylpentane called
isooctane (octane number=100)

(*iii*) **Aromatisation** (also termed *Platforming*). By passing crude naphtha vapours over platinum catalyst ($Pt+Al_2O_3$) at 770K, when straight chain alkanes yield a mixture of benzene, toluene and xylenes (BTX), *e.g.*, heptane (octane number=0) gives toluene (octane number=104). No-lead gasoline sold today is the gasoline obtained by isomerisation and alkylation blended with BTX. Its octane number is about 90.

12. **Cetane Number.**—Working of a diesel engine differs from that of a petrol engine. In a diesel engine air is sucked into the cylinder and then compressed in the ratio 14-17 to 1 when it gets heated. Diesel is then injected into the cylinder in the form of a fine spray when it burns spontaneously. In diesel engines straight-chain hydrocarbons constitute a superior fuel than the branched-chain hydrocarbons.

Quality of diesel fuel is expressed in terms of cetane number. Cetane (*n*-hexadecane, $C_{16}H_{34}$) ignites rapidly and is given arbitrarily a cetane rating of 100. α-Methylnaphthalene ignites slowly and is assigned a cetane rating *zero*.

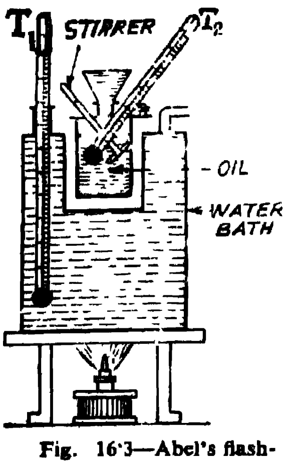


Fig. 16·3—Abel's flash-point apparatus.

Cetane number of a given sample is the percentage of cetane in a cetane and α-methylnaphthalene mixture which compares in ignition quality with the given sample.

13. **Flash Point**—The explosive nature of a liquid hydrocarbon is determined by volatility. It is important, therefore, that kerosene needed for illuminating purposes should not be so volatile as to form explosive mixture with air at ordinary temperature. *The minimum temperature at which an oil gives off enough vapour to form an explosive mixture with air is flash-point or flashing point.* Abel's apparatus used for the determination of flash-point is shown in Fig. 16·3. The sample of kerosene is placed in a small metal cup and heated slowly by means of the surrounding water bath. From time to time, a slit in the cover of the metal cup is opened and a tiny flame introduced momentarily by means of an automatic device. The temperature at which the vapour ignites with a minute explosion is noted and gives the flash-point.

The minimum flash-point permitted in India is 317K, that in France is 306K whereas the one adopted in England is 306·8K.

14. **Petro-Chemical Industry.**—Natural gas is a mixture of alkanes and alkenes. Large volumes of these hydrocarbons are obtained during cracking of petroleum. These constitute excellent raw materials for numerous compounds which are termed *petrochemicals*. Different hydrocarbons of petroleum and various compounds obtained from them are the following :

Hydrocarbons	Compounds obtained
(i) Methane	Mono-, di-, tri-, and tetrachloromethanes, methanol, methanal, acetylene, formic acid, methyl ether, dimethyl sulphate, ethylene glycol, methylamine, haxamethylenetetramine, hydrogen cyanide, acrylonitrile dichloromonofluoromethane, dichlorodifluoromethane.
(ii) Ethane	Ethyl chloride, acetic acid, nitroethane, ethylene, acetaldehyde, acetic anhydride, ethyl acetate, diethyl ether.
(iii) Ethylene	Ethanol, ethylene glycol, ethylene oxide, ethylene chloride, ethylene chlorohydrin, vinyl chloride, butadiene, acetaldehyde, acetic acid, ethyl acetate, ethyl ether, crotonaldehyde, butyraldehyde, 1-butanol, butyric acid, ethyl chloride, tetraethyl lead, ethylene bromide, dithioglycol, glyoxal, acrylonitrile, acrylic acid.
(iv) Propane	Propanol, propionic acid, nitro-methane, nitro-ethane, nitropropane, ethylene, 1, 3-dichloropropane. isopropyl ether, isopropylamines, acetone, acetone cyanohydrin.
(v) Propene	Glycerol, allyl alcohol, allyl chloride, isopropyl alcohol, isopropyl ether, isopropylamine, acetone, acetone cyanohydrin, diacetone alcohol, mesityl oxide, keten, acetylacetone, cumene, propylene oxide, propylene glycol, propionaldehyde, propionic acid, *n*-propyl alcohol, acrolein.
(vi) Butanes	Butylenes, butadiene, thiophene.
(vii) Butenes	Butanol, butadiene, ethyl methyl ketone, butyl ethyl ketone, *tert*-butyl alcohol, polybutylenes, butyl rubber, iso-octane.
(viii) Pentane	Amyl alcohols, amyl chlorides, amylamines, amyl mercaptans pantylenes, amyl phenols.
(ix) *n*-Hexane	Benzene, DDT, gammexane ($C_6H_6Cl_6$).
(x) *n*-Heptane	Toluene.
(xi) Acetylene	Carbon black, vinylacetylene, chloroprene, acetaldehyde, acetic acid, peracetic acid, vinyl chloride, trichloroethane (1, 1, 2-), tetrachloroethane (1, 1, 2, 2-), pentachloroethane, ethylene chloride, trichloroethylene, tetrachloroethylene, vinyl acetate, methyl vinyl ether, butadiene, acrylonitrile.
(xii) Diolefins	Hexamethylenediamine, 4-vinylcyclohexene, isoprene.
(xiii) Cycloalkenes	Benzene, toluene, xylenes, adipic acid, hexamethylenediamine.
(xiv) Toluene	Benzyl chloride, benzal chloride, benzotrichloride, benzyl alcohol, benzaldehyde, benzoic acid, T.N.T., toluenesulphonic acids, *p*-toluenesulphonamide, phthalic anhydride, *tere*-phthalic acid.

QUESTIONS

Essay Type :

1. What are various fractions obtained from Petroleum ? Mention the industrial uses to which they are put. (*Delhi B.Sc. Hons. Sub. 1976 Supp.*)

2. Describe the occurrence, composition and probable origin of natural petroleum. Give an outline, in brief, of the method of treatment of the crude product.

3. Give a short account of the methods employed for the production of synthetic petrol. What attempts are being made in our country for its manufacture ? (*Delhi B.Sc. 1979, 77*)

4. (*a*) How is synthetic petrol made ?

(*b*) What are petrochemicals ? How can teflon and neoprene be prepared from petrochemicals ?

(*c*) How can the octane number of a fuel be improved ? (*Delhi B.Sc. Hons. 1981*)

Short Answer Type :

Write short notes on :

1. Cracking and its importance in petroleum industry. (*Andhra B.Sc. 1978*)

2. Octane number. How can octane number of petrol be increased ?

3. Knocking. (*Delhi B.Sc. 1976 ; B.Sc. Hons. 1977*)

4. Anti-knock compounds.

5. Polymerisation. (*Andhra B.Sc. 1978*)

6. Aviation petrol.

7. Petrol substitutes.

[Hint. See Synthetic Petrol and Power Alcohol.]

8. TEL.

9. Catalytic cracking or Reforming.

10. Sweetening of sour gasoline.

11. Flash-point.

12. Explain the terms, Octane number and Cetane number as used for grading of automobile fuels. (*Delhi B.Sc. Hons. 1978, 76 ; Kerala B.Sc. 1977 ; Kurukshetra 1976*)

13. What are petro-chemicals ? Give examples of three classes of organic compounds included therein. (*Delhi B.Sc. Hons. 1976*)

14. Describe in brief a method for the synthesis of a liquid fuel from water gas. (*Delhi B.Sc. Hons. 1976*)

17

Halogen Derivatives

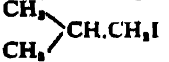
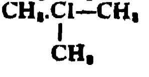
1. General.—The paraffins react with halogens which replace one or more of their hydrogen atoms by halogen atoms. The products obtained are called *halogen derivatives of paraffins*. These are classified as *mono-, di-, tri- and tetra-halogen derivatives* according to the number of halogen atoms in the molecule. All these substances are purely synthetic products and are not found in nature. They are very reactive and provide the starting material for a very large number of aliphatic compounds. These are analogous to inorganic metallic halides such as sodium chloride, NaCl but differ from the latter in being covalent in nature. Thus whereas inorganic chlorides give a white precipitate of AgCl with an aqueous solution of silver nitrate, ethyl chloride gives none.

MONOHALOGEN DERIVATIVES

2. Nomenclature.—The monohalogen derivatives of paraffins may be represented by the general formula C_nH_{2n+1} X or RX where X repesents F, Cl, Br or I.

Monohalogen derivatives are usually named as the halides of the corresponding alkyl groups and the homologous series is known as alkyl halides. These are further named as primary, secondary or tertiary according as the halogen atom is attached to a primary, secondary or tertiary carbon atom.

In the **IUPAC** system alkyl halides are named as substitution products of the corresponding alkanes as given below :

Formula	*Common name*	*IUPAC name*
CH_3Br	Methyl bromide	Bromomethane
$CH_3.CH_2I$	Ethyl iodide	Iodoethane
$CH_3.CH_2.CH_2Cl$	*n*-Propyl chloride	1-Chloropropane
$CH_3.CHCl.CH_3$	Isopropyl chloride	2-Chloropropane
$CH_3.CH_2.CH_2.CH_2I$	*n*-butyl iodide	1-Iodobutane
 $(CH_3)_2CH.CH_2I$	Isobutyl iodide	1-Iodo-2-methylpropane
$CH_3.CH_2.CHI.CH_3$	*sec*-butyl iodide	2-Iodobutane
 $CH_3.CI(CH_3)—CH_3$	*tert*-butyl iodide	2-Iodo-2-methylpropane

3. General Methods of Preparation.—Different methods by which the alkyl halides may be prepared are :

(1) The method most widely used is *by the replacement of the "OH" group in alcohols with an "X" atom by means of* :

(*a*) Hydrogen chloride or bromide in the presence of zinc chloride or sulphuric acid.

$$R|\overline{OH+H}|Cl \xrightarrow{ZnCl_2} RCl + H_2O \qquad (v.g.)$$

$$R|\overline{OH+H}|Br \xrightarrow{H_2SO_4} RBr + H_2O \qquad (ex.)$$

In case of ***secondary*** ***and*** *tertiary alcohols, the* ***sulphuric acid*** *is omitted since it brings about dehydration of alcohols to olefins.* Primary alcohols may be heated with potassium bromide and sulphuric acid.

$$ROH+KBr+H_2SO_4 \longrightarrow RBr+KHSO_4+H_2O \qquad (v.g.)$$

Alkyl iodides are obtained in good yield by refluxing the alcohol with excess of constant boiling hydriodic acid (57 per cent).

(*b*) ***Phosphorus halides.***

$$ROH+PCl_5 \longrightarrow RCl+POCl_3+HCl$$
$$3ROH+PCl_3 \longrightarrow 3RCl+H_3PO_3$$

Phosphorus tri-bromide and tri-iodide are usually prepared *in situ*, bromine or iodine is added to a mixture of red phosphorus and alcohol and warmed. The yield is *v.g.-ex.* for primary alcohols but is less for secondary and still less for tertiary alcohols.

(*c*) ***Thionyl chloride in presence of pyridine*** (*1 mol*).

$$ROH+SOCl_2 \xrightarrow{\text{Reflux}} RCl+SO_2+HCl$$

(2) ***By the addition of halogen acids to an olefin***, *e.g.*,

$$\underset{\text{Ethylene}}{CH_2{=}CH_2}+HI \longrightarrow \underset{\text{Ethyl iodide}}{CH_3.CH_2I}$$

(3) ***By direct halogenation of paraffins in the presence of light or catalysts.*** The order of ease of substitution is

tertiary hydrogen atom>secondary>primary.

During chlorination every possible monochloride is obtained and chlorination beyond monosubstitution may be suppressed by controlling the ratio of chlorine to paraffin.

$$\underset{\text{Methane}}{CH_4} + Cl_2 \xrightarrow{h\nu} \underset{\text{Methyl chloride}}{CH_3Cl} + HCl$$

4. ***By the displacement of one halogen atom by another.*** For example, an iodide may be obtained in many cases by treating the corresponding chloride or bromide in acetone or methanol solution with sodium iodide. This is possible because sodium iodide is soluble in methanol or acetone whereas sodium bromide and sodium chloride are insoluble in these.

$$RCl+NaI \longrightarrow RI+NaCl$$

5. General Properties of the Alkyl Halides.—

(*a*) **Physical.** (*i*) The lower members (methyl chloride, methyl bromide and ethyl chloride) are gases. The rest of the lower members are colourless, sweet smelling liquids.

(*ii*) They are generally insoluble in water but are soluble in alcohol, ether and benzene.

(*iii*) Bromides and iodides are heavier than water.

(*iv*) Their boiling points and densities show a regular gradation in the order iodide>bromide>chloride>fluoride.

(*v*) Alkyl iodides are sufficiently reactive to be decomposed by light. Liberation of iodine is responsible for the darkening of alkyl iodides on standing. This is due to the instability of C—I bond.

$$2RI \longrightarrow R-R+I_2$$

(*vi*) *Spectroscopic Properties.* In the UV region alkyl halides show absorption bonds of low intensity as follows :

$$C-Cl=173m\mu, \quad C-Br=240m\mu$$

and $C-I=258m\mu$

The IR absorption region of alkyl halides (C—X stretch) depends on the nature of the halogen atom :

C—F, 1100—1000 cm^{-1}(s) ; C—Cl, 750—700 cm^{-1}(s) ;
C—Br, 600—500 cm^{-1}(s) ; C—I, 500 cm^{-1}(s).

In the NMR spectra proton signal of methylene group attached to the halogen atom has a chemical shift value in the range 3·2—3·78 (τ 6·8—6·3).

(*b*) **Chemical.** The alkyl halides are highly reactive, the order of reactivity being iodide>bromide>chloride (*nature of the halogen atom*) for a particular alkyl group and tertiary > secondary > primary > methyl halide (*nature of the alkyl group*) for a particular halogen atom. Amongst the primary halides the order of reactivity is

$$CH_3X>C_2H_5X>C_2H_5CH_2X, \text{ etc.}$$

These orders of reactivity and other important reactions of alkyl halides can be explained in the terms of the nature of C—X bond which is highly polarised covalent bond due to large electronegativity difference between C and X atoms. In the dipole, carbon is the positive end and halogen is the negative end.

(*i*) The $C^{\delta+}$ is susceptible to attack by nucleophiles.* Presence of a small negative charge on the halogen atom (X) facilitates its leaving as halide ion (X^-) when the molecule is approached by a nucleophile. Leaving halide ion is substituted by the approaching nucleophile (an electron-rich species). This gives rise to **nucleophilic substitution reactions** of alkyl halides.

$$Nu^- + R-X \longrightarrow Nu-R+X^- \qquad (\textit{Nucleophilic substitution})$$

$$R-X \xrightarrow[\text{slow}]{-X^-} R^+ \xrightarrow{Nu^-} R-Nu \qquad (S_N1 \text{ reaction})$$

$$Nu^- + R-X \xrightarrow{\text{slow}} \overset{\delta-}{Nu}\ldots R\ldots\overset{\delta-}{X} \rightarrow Nu-R + X^- \qquad (S_N2 \text{ reaction})$$

(*ii*) The positive charge on carbon is propagated to the neighbouring carbon atoms by inductive effect. When approached by a stronger base, it tends to lose a proton usually from the β-carbon atom. Such reactions involving the elimination of a halogen atom along with a proton from β-position are termed **elimination reactions**.

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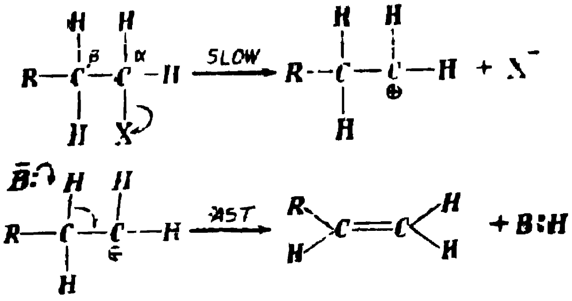
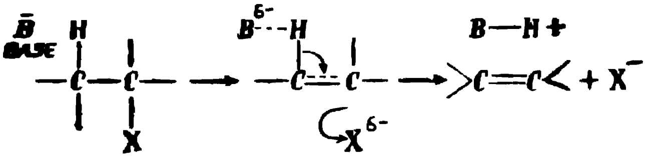
*Some typical nucleophiles in the increasing order of **nucleophilicity** (*defined as the ability to coordinate with an electron-deficient C atom*) are :
H_2O, NO_3^-, F^-, CH_3COO^-, Cl^-, ^-OR, Br^-, N_3^-, ^-OH, ^-CN, I^-, ^-SH, ^-SR.

(*a*) E1 *reaction*



(*b*) E2 *reaction*



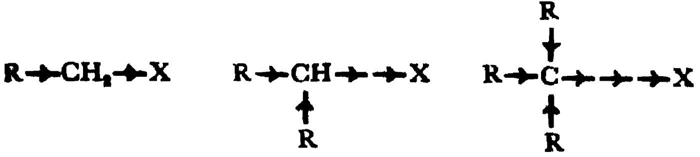
TRANSITION STATE

As the reactions of alkyl halide involve leaving of X⁻, the difference in the reactivity of various halogens should be in the order of decrease of C—X bond strength. This has actually been found to be the case.

Type of bond	C—F	C—Cl	C—Br	C—I
Bond energy (kJ mol^{-1})	447·7	326·4	284·5	213·4

Variation of activity with the nature of alkyl group (tertiary > secondary > primary) can be explained as follows :

The alkyl groups are electrons repelling or electron releasing. Larger the number of alkyl groups attached to the carbon atom of the C—X, the greater is the electron density on this carbon atom and hence greater is the repulsion of the electron pair towards the X-atom of the C—X bond. This may be represented qualitatively as follows :



$$R\rightarrow CH_2\rightarrow X \qquad R\rightarrow \underset{\underset{R}{\uparrow}}{CH}\rightarrow\rightarrow X \qquad R\rightarrow \overset{\overset{R}{\downarrow}}{\underset{\underset{R}{\uparrow}}{C}}\rightarrow\rightarrow\rightarrow X$$

Thus the X atom is released as an X⁻ ion most readily in tertiary halides and least readily in primary halides.

The primary alkyl halides undergo reactions by either S_N2 or E2 mechanism which involve the formation of an intermediate transition state. Bulkier groups cause steric hindrance in the formation of transition state. Hence ease of formation of transition state decreases as we pass from simple methyl group to bulky *n*-propyl group. Therefore, the order of reactivity should be :

$$CH_3X > C_2H_5X > n\text{-}C_3H_7X, \text{ etc.}$$

The tertiary alkyl halides react by either S_N1 or E1 mechanism *via* formation of a carbonium ion as intermediate. The reaction is, therefore, favoured by structural features which help stabilization of the intermediate carbocation.

The secondary alkyl halides react by either or both of these mechanisms depending on the nature of alkyl halide and the nature of reagents.

Many of the alkyl halides burn with green edged flame. They are extremely important reagents in organic syntheses as they undergo a large variety of reactions given below :

(1) Nucleophilic Substitution Reactions

(*i*) HYDROLYSIS. Alkyl halides are hydrolysed to ***alcohols*** very slowly by water but rapidly by boiling with aqueous alkalis or with silver oxide suspended in boiling water.

$$\underset{}{R\bar{X}} + \underset{(Aqueous)}{\overset{+}{K}\,\overline{O}H} \longrightarrow \underset{\text{Alcohol}}{ROH} + KX$$

or $$RX + {}^{-}OH \longrightarrow ROH + X^{-}$$

(*ii*) REACTION WITH SODIO-ALKYNIDES. **Higher alkynes** are produced when alkyl halides react with sodio-alkynides.

$$\underset{\text{Sodio alkynide}}{RC{\equiv}C|\overline{Na} + \underline{I}|R'} \longrightarrow \underset{\text{Higher alkyne}}{RC{\equiv}CR'} + NaI$$

or $$R{-}X + :\bar{C}{\equiv}CH \longrightarrow RC{\equiv}CH + X^{-}$$

Reaction is practically limited to the use of primary alkyl halides because of the great tendency of secondary and tertiary alkyl halides to undergo elimination.

$$\underset{sec\text{-Propyl halide}}{(CH_3)_2CHX} + :\bar{C}{\equiv}CH \longrightarrow \underset{\text{Propylene }(Olefin)}{CH_3.CH{=}CH_2} + HC{\equiv}CH + X^{-}$$

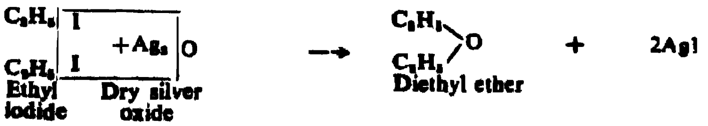
Order of reactivity of alkyl halides for elimination is 3° > 2° > 1° while that for substitution is 1° > 2° > 3°, *i.e.*, elimination increases and substitution decreases as we pass from primary to secondary to tertiary halides.

$$RX = \underset{\textit{Substitution increases}}{\underleftarrow{\overset{\textit{Elimination increases}}{\overrightarrow{1^\circ \quad 2^\circ \quad 3^\circ}}}} \qquad \begin{matrix} \textit{Elimination} & (E2) \\ vs. & \\ \textit{Substitution} & (S_N2) \end{matrix}$$

(*iii*) REACTION WITH SODIUM ALKOXIDE OR DRY SILVER OXIDE. Alkyl halides react with sodium alkoxide or dry silver oxide to give ethers.

$$\underset{\text{Sod. alkoxide}}{RO\overline{Na}} + \underset{\text{Alkyl halide}}{\overline{X}|R'} \longrightarrow \underset{\text{Ether}}{ROR'} + NaX$$

$$\underset{\text{Sodium ethoxide}}{C_2H_5O|\overline{Na}} + \underset{\text{Ethyl iodide}}{\overline{I}|C_2H_5} \longrightarrow \underset{\text{Diethyl ether}}{C_2H_5.OC_2H_5} + NaI$$



$$\underset{\text{Ethyl iodide}}{\begin{matrix} C_2H_5|I \\ C_2H_5|I \end{matrix}} + \underset{\text{Dry silver oxide}}{Ag_2|O} \longrightarrow \underset{\text{Diethyl ether}}{\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\!\!>O} + 2AgI$$

Reaction with sodium alkoxide is an example of S_N2 reaction and takes place as under :

$$\underset{}{C_2H_5O^- + CH_3{-}I} \longrightarrow \underset{\text{Transition state}}{C_2H_5O\,..CH_3...I} \longrightarrow C_2H_5O{-}CH_3 + I^-$$

(*iv*) REACTION WITH POTASSIUM CYANIDE. **Alkyl cyanides** are obtained when alkyl halides are heated with aqueous cyanide, a small amount of isocyanide is also obtained.

$$\underset{\text{Alkyl halide}}{R\boxed{X \;+\; K}CN} \longrightarrow \underset{\text{Alkyl cyanide}}{RCN} + KX$$

or $$R{-}X + :C{\equiv}N \longrightarrow RC{\equiv}N + X^-$$

Alkyl cyanides are very important compounds since they can be used to prepare many other compounds, *e.g.*,

(*a*) **Acids** are obtained by hydrolysis of cyanides with mineral acids or alkalis.

$$\underset{\text{Alkyl cyanide}}{RC{\equiv}N} \xrightarrow{H_2O} \underset{\text{Amide}}{RCONH_2} \xrightarrow{H_2O} \underset{\text{Acid}}{RCOOH} + NH_3 \quad (g.\text{-}v.g.)$$

$$\underset{\text{Methyl cyanide}}{CH_3C{\equiv}N} \xrightarrow{H_2O} \underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow{H_2O} \underset{\text{Acetic acid}}{CH_3COOH} + NH_3$$

(*b*) **Amides** are obtained by the partial hydrolysis of cyanides with alkaline hydrogen peroxide.

$$R.C{\equiv}N + H_2O \xrightarrow{\text{alk } H_2O_2} RCONH_2$$

$$\underset{\text{Methyl cyanide}}{CH_3.C{\equiv}N} + H_2O \longrightarrow \underset{\text{Acetamide}}{CH_3CONH_2}$$

(*c*) **Primary amines** are obtained by the reduction of cyanides with nascent hydrogen from sodium and ethanol.

$$\underset{\text{Alkyl cyanide}}{R.C{\equiv}N} + 4[H] \rightarrow \underset{\text{Primary amine}}{RCH_2NH_2}$$

$$\underset{\text{Methyl cyanide}}{CH_3.C{\equiv}N} + 4[H] \rightarrow \underset{\text{Ethylamine}}{CH_3.CH_2NH_2}$$

(*v*) REACTION WITH SILVER CYANIDE. **Alkyl isocyanides** are obtained when alkyl halides are heated with aqueous ethanolic silver cyanide. Isomeric cyanides are also formed in small amounts.

$$C_2H_5\boxed{I \;+\; Ag}CN \longrightarrow \underset{\text{Ethyl isocyanide}}{C_2H_5NC} + AgI$$

Silver cyanide, Ag—C≡N : is a covalent compound. When treated with an alkyl halide, the potential alkyl carbonium ion is driven to the nitrogen to yield mainly alkyl isocyanide (*cf.* KCN which is an ionic compound and gives R—C≡N as explained above).

$$Ag{-}C{\equiv}N: + R{-}I \longrightarrow [Ag{-}C{\equiv}N{-}R]^+I^- \xrightarrow{-AgI} \underset{\text{Alkyl isocyanide}}{R{-}N{\rightleftharpoons}C:}$$

(*vi*) REACTION WITH SILVER SALT OF A FATTY ACID. **Esters** are obtained when alkyl halides are heated with an ethanolic solution of the silver salt of a fatty acid.

$$\mathrm{RCOO\overline{|Ag\ \ +\ \ X|}R'} \longrightarrow \mathrm{RCOOR'} + \mathrm{AgX}$$

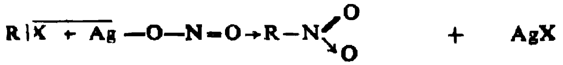
Silver salt of a fatty acid — Alkyl halide — Ester

$$\mathrm{CH_3COO\overline{|Ag\ \ +\ \ I|}C_2H_5} \longrightarrow \mathrm{CH_3COOC_2H_5} + \mathrm{AgI}$$

Silver acetate — Ethyl iodide — Ethyl acetate (*An ester*)

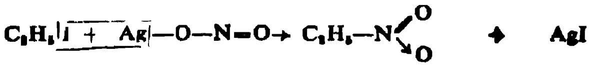
$$\text{or} \quad \mathrm{RCO\bar{O}} + \mathrm{R'X} \longrightarrow \mathrm{RCOOR'} + \mathrm{\bar{X}}$$

(*vii*) REACTION WITH SILVER NITRITE. On heating an alkyl halide with an aqueous ethanolic solution of silver nitrite, **Nitroparaffin** is obtained as the main product. Some alkyl nitrite is also obtained.



$$\mathrm{R\overline{|X\ +\ Ag}{-}O{-}N{=}O} \rightarrow \mathrm{R{-}N}\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix} + \mathrm{AgX}$$

Nitroparaffin



$$\mathrm{C_2H_5\overline{|I\ +\ Ag|}{-}O{-}N{=}O} \rightarrow \mathrm{C_2H_5{-}N}\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix} + \mathrm{AgI}$$

Nitroethane

(*viii*) REACTION WITH POTASSIUM NITRITE. By heating an alkyl halide with potassium nitrite in an aqueous ethanolic solution, **Alkyl nitrite** is obtained as the main product though some nitroparaffin is also obtained.

$$\mathrm{R\overline{|X\ \ +\ \ K|}{-}O{-}N{=}O} \rightarrow \mathrm{R{-}O{-}N{=}O} + \mathrm{KX}$$

Alkyl nitrite

$$\mathrm{C_2H_5I} + \mathrm{K{-}O{-}N{=}O} \rightarrow \mathrm{C_2H_5{-}O{-}N{=}O} + \mathrm{KI}$$

Ethyl nitrite

$$\text{or} \quad \mathrm{C_2H_5I} + \mathrm{\bar{O}{-}N{=}O} \rightarrow \mathrm{C_2H_5O{-}N{=}O} + \mathrm{\bar{I}}$$

(*ix*) REACTION WITH SODIUM HYDROGEN SULPHIDE. Alkyl halides form **thioalcohols** with aqueous alcoholic sodium hydrogen sulphide.

$$\mathrm{R\overline{|X\ \ +\ \ Na|}SH} \longrightarrow \mathrm{RSH} + \mathrm{NaX}$$

Alkyl halide — Sod. hydrogen sulphide — Thioalcohol

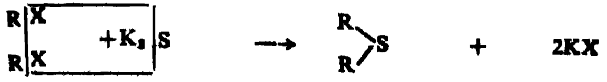
$$\text{or} \quad \mathrm{R{-}X} + \mathrm{:SH^-} \longrightarrow \mathrm{RSH} + \mathrm{X^-}$$

(*x*) REACTION WITH MERCAPTIDES. Alkyl halides when heated with an alcoholic solution of a mercaptide (metallic derivative of a thioalcohol) or with potassium sulphide form **thioethers.**

$$\mathrm{RS\overline{|Na\ \ +\ \ X|}R'} \longrightarrow \mathrm{RSR'} + \mathrm{NaX}$$

Sod. mercaptide — Thioether

$$\text{or} \quad \mathrm{R\bar{S}} + \mathrm{R'X} \longrightarrow \mathrm{RSR'} + \mathrm{\bar{X}}$$



$$\begin{matrix}\mathrm{R|X}\\ \mathrm{R|X}\end{matrix}\ \boxed{+\mathrm{K_2}}\ \mathrm{|S} \longrightarrow \begin{matrix}\mathrm{R}\searrow\\ \mathrm{R}\nearrow\end{matrix}\mathrm{S} + \mathrm{2KX}$$

Thioether

(*xi*) REACTION WITH AMMONIA. When alkyl halides are heated with ethanolic solution of ammonia under pressure in a sealed tube, a mixture of **Amines** (*substituted ammonias*) is obtained. For example,

$$C_2H_5\boxed{I + H}\underset{\text{Ammonia}}{NH_2} \rightarrow \underset{\substack{\text{Ethylamine}\\ (\textit{Primary amine})}}{C_2H_5NH_2} + HI$$

$$\underset{\text{Ethylamine}}{C_2H_5NH}\boxed{H + I}C_2H_5 \rightarrow \underset{\substack{\text{Diethylamine}\\ (\textit{Secondary amine})}}{(C_2H_5)_2NH} + HI$$

$$(C_2H_5)_2N\boxed{H + I}C_2H_5 \rightarrow \underset{\substack{\text{Triethylamine}\\ (\textit{Tertiary amine})}}{(C_2H_5)_3N} + HI$$

$$(C_2H_5)_3N + C_2H_5I \rightarrow \underset{\substack{\text{Tetraethylammonium iodide}\\ (\textit{Quaternary compound})}}{(C_2H_5)_4NI}$$

or $$C_2H_5\text{—}X + :NHR_2 \rightarrow \underset{\text{Amine salt}}{C_2H_5\overset{+}{N}HR_2} + \overset{-}{X}$$

[where R = H and/or alkyl group]

(2) **Elimination Reaction or Dehydrohalogenation.** When alkyl halides are boiled with alcoholic potash, **olefins** are obtained, *e.g.*, propyl bromide gives propylene.

$$\underset{\text{Alkyl halide}}{C_nH_{2n+1}X} + \underset{(\textit{Alcoholic})}{KOH} \longrightarrow \underset{\text{Olefin}}{C_nH_{2n}} + KX + H_2O$$

$$\underset{\text{Propyl bromide}}{CH_3.CH_2.CH_2Br} + \underset{(\textit{Alcoholic})}{KOH} \longrightarrow \underset{\text{Propylene}}{CH_3.CH{=}CH_2} + KBr + H_2O$$

In fact on heating an alkyl halide with an alkali (aqueous or alcoholic), three products are obtained : alcohol, olefin and ether. An alcohol is the main product with aqueous alkali or moist silver oxide (AgOH) and an olefin is the main product with alcoholic alkali.

Ethanolic potassium hydroxide always contains some potassium ethoxide which reacts with alkyl halide to give ether.

$$\underset{\text{Pot. ethoxide}}{C_2H_5O}\boxed{K + I}C_2H_5 \rightarrow \underset{\text{Ethyl ether}}{C_2H_5\text{—}O\text{—}C_2H_5} + KI$$

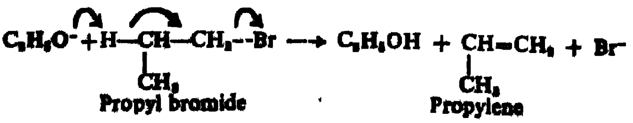
Similarly, methyl iodide with methanolic potash gives methyl ether and no olefin.

$$\underset{\text{Pot. ethoxide}}{CH_3O}\boxed{K + I}CH_3 \rightarrow \underset{\text{Methyl ether}}{CH_3OCH_3} + KI$$

With ethyl halide, yield of ethylene under most favourable conditions is only 1 per cent, the main products being substitution products.

The mechanism of the reaction involving elimination of a molecule of HX to form an olefin is as follows :

Ethanolic potassium hydroxide contains potassium ethoxide which reacts with alkyl halide. The reaction is bimolecular and takes place by an E2 mechanism.



$$C_2H_5O^- + H\text{—}\underset{\substack{|\\ CH_3}}{CH}\text{—}CH_2\text{—}Br \longrightarrow C_2H_5OH + \underset{\substack{|\\ CH_3}}{CH}{=}CH_2 + Br^-$$

Propyl bromide Propylene

Olefins obtained above may be used for the preparation of acetylenes as follows :

$$\underset{\text{Propylene}}{CH_3CH{=}CH_2} \xrightarrow{Br_2} \underset{\text{Propylene bromide}}{CH_3.CHBr.CH_2Br} \xrightarrow[\text{alcoholic}]{KOH} \underset{\text{Propyne}}{CH_3.C{\equiv}CH}$$

(3) **Reduction.** Alkyl halides are reduced by zinc-copper couple, sodium and ethanol or tin and hydrochloric acid, etc., to form the corresponding paraffins as a result of electron transfer from the metal to the substrate.

$$\underset{\text{from Zn/Cu couple}}{Zn} \rightarrow Zn^{2+} + \underset{\text{electron}}{2e^-}$$

$$RX + e^- \rightarrow \bar{X} + R^{\cdot} \xrightarrow{e^-} \bar{R}:$$

$$\bar{R}: + C_2H_5OH \rightarrow R{-}H + C_2H_5O^-$$

Alkyl iodides may also be reduced by heating with concentrated hydriodic acid in the presence of red phosphorus at 430K.

$$C_2H_5I + HI \rightarrow \underset{\text{Ethane}}{C_2H_6} + I_2$$

(4) **Wurtz Reaction.** An ethereal solution of an alkyl halide (preferably bromide or iodide) gives a **paraffin** when heated with metallic sodium.

$$R\boxed{X + 2Na + X}R' \rightarrow R{-}R' + 2NaX$$

$$CH_3\boxed{I + 2Na + I}CH_3 \rightarrow \underset{\text{Ethane}}{CH_3{-}CH_3} + 2NaI$$

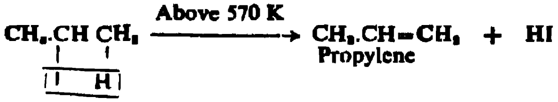
(5) **Reaction with Magnesium.** Alkyl halides are used to prepare **Grignard reagents** by reaction with dry magnesium powder in dry ether or dioxan.

$$\underset{\text{Dry alkyl halide}}{RX} + \underset{\text{dry}}{Mg} \xrightarrow{\text{dry ether}} \underset{\text{Grignard reagent}}{R{-}Mg{-}X}$$

$$C_2H_5I + Mg \xrightarrow{\text{dry ether}} \underset{\text{Ethylmagnesium iodide}}{C_2H_5{-}Mg{-}I}$$

Grignard reagents are very important, being used for the preparation of a very large number of organic compounds.

(6) **Action of Heat.** (*a*) When heated at a temperature above 570K, alkyl halides tend to lose a molecule of halogen acid and give olefins. For example, isopropyl iodide gives propylene.



$$CH_3.\underset{|}{\overset{}{CH}}\,\underset{|}{CH_2} \xrightarrow{\text{Above 570 K}} \underset{\text{Propylene}}{CH_3.CH{=}CH_2} + HI$$

$$\boxed{I \quad H}$$

In their tendency to lose a molecule of halogen acid the alkyl halides can be arranged as under :

Iodide > Bromide > Chloride, and

Tertiary halides > Secondary > Primary.

Thus tertiary iodides lose a molecule of HI in no time.

(b) **When heated at about 570K or at a lower temperature in the presence of aluminium chloride as catalyst, the alkyl halides undergo** rearrangement, *e.g.*, 1-bromobutane gives 2-bromobutane.

$$\underset{\text{1-bromobutane}}{CH_3.CH_2.CH_2.CH_2.Br} \xrightarrow[AlCl_3]{570K} \underset{\text{2-bromobutane}}{CH_3.CH_2.CHBr.CH_3}$$

Mechanism of the Reaction :

$$\underset{\text{1-Bromobutane}}{CH_3CH_2CH_2CH_2Br} \xrightarrow{-Br^-} \underset{\text{1°carbocation}}{CH_3CH_2CH_2\overset{+}{C}H_2} \xrightarrow[\text{Hydride shift}]{\text{Rearrangement}}$$

$$\underset{\substack{\text{More stable}\\ \text{2°carbocation}}}{CH_3CH_2\overset{+}{C}HCH_3} \xrightarrow{Br^-} \underset{\text{2-Bromobutane}}{CH_3CH_2CHBrCH_3}$$

In case there is no hydrogen atom attached to the carbon atom **next** to C—X group an alkyl group migrates as in neopentyl chloride **which** gives 2-chloro-2-methylbutane on heating.

$$(CH_3)_3C.CH_2Cl \longrightarrow (CH_3)_2.CCl.CH_2.CH_3$$

Mechanism of the Reaction

$$(CH_3)_3C-CH_2Cl \xrightarrow{Cl^-} \underset{\text{1° carbocation}}{(CH_3)_3C-\overset{+}{C}H_2} \xrightarrow[\text{Alkyl shift}]{\text{Rearrangement}}$$

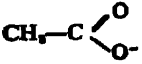
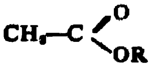
$$\underset{\text{3° carbocation}}{(CH_3)_2\overset{+}{C}-CH_2.CH_3} \xrightarrow{Cl^-} (CH_3)_2CCl.CH_2CH_3$$

5. Reactions of Alkyl halides (Revision)

(a) Nucleophilic substitution. The nucleophile may be an anion, $\bar{Y}$: a **neutral** molecule, Y: or HY: and the operation of each is illustrated in the **general** equations for a compound RX given below :

$$R-X + \bar{Y}: \rightarrow R-Y + \bar{X}$$

$$R-X + HY: \rightarrow R\overset{+}{Y}H + \bar{X}: \rightarrow RY: + HX$$

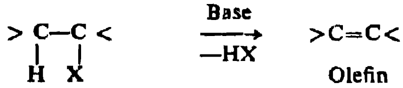
Nucleophile	*Product*	*Product name* (when R is CH_3)
(1) *When* $\bar{Y}$: *is an ion* :		
$:\bar{O}H$	ROH	methyl alcohol
$:\bar{O}CH_3$	$ROCH_3$	dimethyl ether
$:\bar{C}\equiv CH$	$RC\equiv CH$	methylacetylene
$:\bar{I}$	RI	methyl iodide
$:\bar{C}\equiv N$	RCN	methyl cyanide
 $CH_3-C\begin{matrix}\diagup O\\ \diagdown O^-\end{matrix}$	 $CH_3-C\begin{matrix}\diagup O\\ \diagdown OR\end{matrix}$	methyl acetate
$:\bar{N}H_2$	RNH_2	methylamine
$:\bar{N}HR$	R_2NH	dimethylamine

$:\bar{N}R_3$	R_3N	trimethylamine
$:\bar{S}H$	RSH	methyl thioalcohol
$:\bar{S}CH_3$	$RSCH_3$	dimethyl thioether
$:\bar{N}O_2$	RNO_2	nitromethane

(2) *When Y: or HY: is a neutral molecule*

$(CH_3)_3N:$	$R\overset{+}{N}(CH_3)_3X^-$	tetramethylammonium halide
HNH_2 [ammonia]	RNH_2	methylamine

(*b*) **Dehydrohalogenation (Elimination) :**



$$\underset{\substack{|\quad\ |\\ H\quad X}}{>C-C<} \xrightarrow[-HX]{\text{Base}} \underset{\text{Olefin}}{>C=C<}$$

(*c*) **Reduction** ·

Catalytic : $RX+H_2 \xrightarrow{Ni} RH + HX$

Chemical : $RX+M+H^+ \longrightarrow RH+M^{++}+X^-$

(*d*) **Preparation of Grignard reagent :**

$$RX+Mg \longrightarrow RMgX$$

SOME INDIVIDUAL MEMBERS

6. Methyl Chloride, Chloromethane, CH_3Cl.—

Preparation. Methyl chloride is prepared industrially :

(*i*) *By passing hydrochloric acid gas through methanol in the presence of anhydrous zinc chloride* :

$$\underset{\text{Methanol}}{CH_3\boxed{OH \quad + \quad H}Cl} \xrightarrow{ZnCl_2} \underset{\text{Methyl chloride}}{CH_3Cl} \quad + \quad H_2O$$

(*ii*) *By heating under pressure trimethylamine hydrochloride with hydrochloric acid.*

$$\underset{\substack{\text{Trimethylamine}\\ \text{hydrochloride}}}{(CH_3)_3N.HCl} + 3HCl \longrightarrow \underset{\substack{\text{Methyl}\\ \text{chloride}}}{3CH_3Cl} + NH_4Cl$$

(*iii*) *By chlorination of methane.* All the four chloromethanes are obtained on chlorination of methane. The chlorine is diluted with nitrogen in the volume ratio $CH_4 : Cl_2 : N_2 : : 8 : 1 : 80$ and the reaction is carried out in the presence of partly reduced cupric chloride. In this way about 20 per cent of the chlorine is used for the preparation of methyl chloride.

$$CH_4+Cl_2+[N_2] \rightarrow CH_3Cl+HCl+[N_2+CH_2Cl_2+CHCl_3+CCl_4]$$

Any one of the four chloromethanes can be obtained as the main product by adjusting the ratio of chlorine to methane.

Properties and Uses. Methyl chloride is a colourless, sweet-smelling gas (b.p. 249K). It is fairly soluble in water and readily soluble in ethanol. It gives all the reactions typical of alkyl halides.

It is used (*i*) in the manufacture of aniline dyes, (*ii*) as a refrigerating agent, (*iii*) as a local anaesthetic, and (*iv*) as a fire extinguisher.

7. Ethyl Chloride, Chloroethane, C_2H_5Cl.—

Preparation. Ethyl chloride is manufactured :

(*i*) *By passing hydrochloric acid gas through ethanol in the presence of anhydrous zinc chloride.*

$$C_2H_5\overline{|OH \quad + \quad \underline{H}}|Cl \xrightarrow{ZnCl_2} C_2H_5Cl + H_2O$$

It can be prepared in the laboratory by the same method.

(*ii*) By the addition of hydrochloric acid to ethylene (from cracked petroleum) in the presence of aluminium chloride as catalyst.

$$\underset{\text{Ethylene}}{CH_2{=}CH_2} + HCl \xrightarrow{AlCl_3} \underset{\text{Ethyl chloride}}{CH_3CH_2.Cl}$$

Properties and Uses. Ethyl chloride is a colourless, pleasant-smelling gas (b.p. 285·5K) and gives all the reactions typical of an alkyl halide.

It is used as a refrigerating agent, local anaesthetic and in the preparation of tetraethyl lead, sulphonal, etc.

8. Ethyl Bromide, Bromoethane, C_2H_5Br. –

Preparation. Ethyl bromide is prepared in the laboratory :

(*i*) *By the action of phosphorus and bromine on ethyl alcohol.*

$$P_4 + 6Br_2 \longrightarrow 4PBr_3$$

$$\underset{\text{Ethanol}}{3C_2H_5OH} + PBr_3 \longrightarrow \underset{\text{Ethyl bromide}}{3C_2H_5Br} + H_3PO_3$$

(*ii*) *By heating together a mixture of ethanol and potassium bromide with concentrated sulphuric acid.*

$$2KBr + H_2SO_4 \longrightarrow K_2SO_4 + 2HBr$$

$$\underset{\text{Ethanol}}{C_2H_5}\overline{\underline{|OH \quad + \quad H}}|Br \longrightarrow \underset{\substack{\text{Ethyl}\\ \text{bromide}}}{C_2H_5Br} + \underset{\substack{\text{Removed by excess}\\ \text{of conc. } H_2SO_4}}{H_2O}$$

Ethyl bromide is, however, prepared industrially by the action of hydogen bromide on ethylene (from cracked petroleum).

$$\underset{\text{Ethylene}}{CH_2{=}CH_2} + HBr \longrightarrow \underset{\text{Ethyl bromide}}{CH_3.CH_2Br}$$

Properties and Uses. Ethyl bromide is a colourless, pleasant-smelling liquid (b.p. 311K). It gives the usual reactions of an alkyl halide and is used as local anaesthetic and in organic synthesis.

9. Ethyl Iodide, Iodoethane, C_2H_5I.—

Preparation. Ethyl iodide is prepared in the laboratory by the action of phosphorus and iodine on ethyl alcohol.

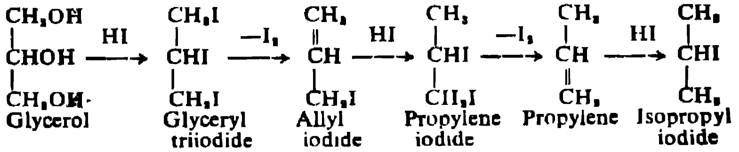
$$P_4 + 6I_2 \longrightarrow 4PI_3$$

$$3C_2H_5OH + PI_3 \longrightarrow 3C_2H_5I + H_3PO_3$$

Properties and Uses. Ethyl iodide is a colourless, sweet-smelling liquid (b.p. 345·5K). It is a typical alkyl halide and is an important synthetic agent.

10. Isopropyl Iodide, 2-iodopropane, $CH_3.CHI.CH_3$.—

Preparation. Isopropyl iodide is prepared by the action of hydriodic acid or phosphorus and iodine (taken in excess) on glycerol.



$$CH_2OH.CHOH.CH_2OH \xrightarrow{HI} CH_2I.CHI.CH_2I \xrightarrow{-I_2} CH_2{=}CH.CH_2I \xrightarrow{HI} CH_3.CHI.CH_2I \xrightarrow{-I_2} CH_3.CH{=}CH_2 \xrightarrow{HI} CH_3.CHI.CH_3$$

Properties and Uses. It is a colourless liquid (b.p. 362·15K) when pure. It is heavier than water (sp. gr. 1·703). It finds use in organic synthesis.

DIHALOGEN DERIVATIVES

11. Nomenclature.—The dihalogen derivatives of paraffins are obtained by the replacement of two hydrogen atoms by two halogen atoms and can be represented by the general formula $C_nH_{2n}X_2$. When the two halogen atoms are attached to the same carbon atom, *i.e.*, are in the *geminal* (*gem*) position, the derivatives are called *alkylidene halides*, *e.g.*, $CH_3.CHBr_2$, ethylidene bromide ; $CH_3.CCl_2.CH_3$, isopropylidene chloride.

When the two halogen atoms are on adjacent carbon atoms, *i.e.*, in the *vicinal* (*vic*) position, the derivatives are named as *alkylene halides*—the halides of the olefins from which these may be prepared by the addition of halogen. For example, $CH_2Br.CH_2Br$ is ethylene bromide and $CH_3.CHCl.CH_2Cl$ is propylene chloride.

When there is one halogen atom attached to each of terminal carbon atoms of the chain, *i.e.*, in the $\alpha\omega$ position, the derivative is named as polymethylene halide. For example,

$CH_2Br.CH_2.CH_2.CH_2.Br$ is tetramethylene bromide.

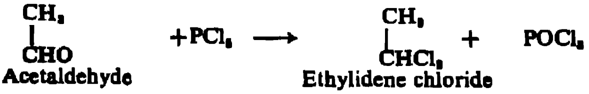
The three types of dihalides and others not covered by these types may also be named by the IUPAC system. For example,

Formula	*Common name*	*IUPAC name*
$CH_2Br.CH_2Br$	Ethylene bromide	1, 2-dibromoethane
$CH_3.CHBr_2$	Ethylidene bromide	1. 1-dibromethane
$CH_3.CHCl.CH_2Cl$	Propylene chloride	1, 2-dichloropropane
$CH_3.CBr_2CH_3$	Isopropylidene bromide	2, 2-dibromopropane
$CH_2Cl.CH_2.CH_2Cl$	Trimethylene chloride	1, 3-dichloropropane
$CH_3.CHBr.CH_2.CH_2Br$	———	1, 3-dibromobutane

12. General Methods of Preparation.—

Alkylidene halides may be prepared :

(*i*) ***By the action of phosphorus pentahalide on aldehyde or Ketones.*** For example,

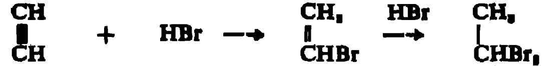


$$CH_3.CHO + PCl_5 \longrightarrow CH_3.CHCl_2 + POCl_3$$

$CH_3.CO.CH_3$ + PCl_5 ⟶ $CH_3.CCl_2.CH_3$ + $POCl_3$

Acetone isopropylidene chloride

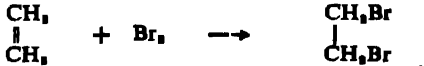
(*ii*) ***By the addition of halogen acid to acetylenes***, *e.g.*,



$$\begin{matrix} CH \\ \| \\ CH \end{matrix} + HBr \longrightarrow \begin{matrix} CH_2 \\ \| \\ CHBr \end{matrix} \xrightarrow{HBr} \begin{matrix} CH_3 \\ | \\ CHBr_2 \end{matrix}$$

Acetylene — Vinyl bromide — Ethylidene bromide

Alkylene halides *are prepared by the addition of halogens to olefins*. For example,



$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + Br_2 \longrightarrow \begin{matrix} CH_2Br \\ | \\ CH_2Br \end{matrix}$$

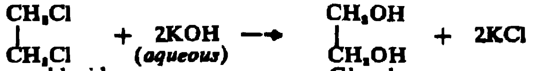
Ethylene — Ethylene bromide

$CH_3CH{=}CH_2 + Br_2 \longrightarrow CH_3.CHBr.CH_2Br$

Propylene — Propylene bromide

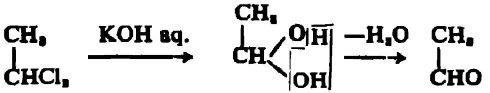
13. General Properties and Reactions.—The dihalides are colourless, sweet-smelling liquids. Alkylidene halides are not as reactive as alkyl halides. It is found that reactivity of chlorine decreases progressively from methyl chloride to methylene chloride, chloroform and carbon tetrachloride. On the other hand, alkylene halides are as reactive as the alkyl halides. Some important reactions of the three classes of dihalides are :

(*i*) ***Hydrolysis***. On hydrolysis with aqueous alkali, alkylene halides give glycols whereas aldehydes or ketones are produced with alkylidene halides.



$$\begin{matrix} CH_2Cl \\ | \\ CH_2Cl \end{matrix} + \underset{(aqueous)}{2KOH} \longrightarrow \begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix} + 2KCl$$

Ethylene chloride — Glycol

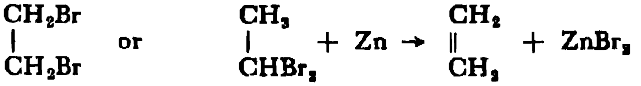


$$\begin{matrix} CH_3 \\ | \\ CHCl_2 \end{matrix} \xrightarrow{KOH\ aq.} \begin{matrix} CH_3 \\ | \\ CH(OH)_2 \end{matrix} \xrightarrow{-H_2O} \begin{matrix} CH_3 \\ | \\ CHO \end{matrix}$$

Ethylidene chloride — Unstable *dihydric alcohol — Acetaldehyde

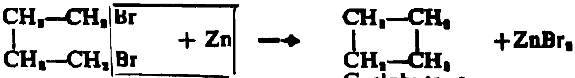
(*ii*) ***Reaction with alcoholic potash***. Alkylene and alkylidene halides yield acetylenes when heated with alcoholic potash (*see* page 2·61).

(*iii*) ***Reaction with zinc dust and Methanol***. Alkylene and alkylidene halides give olefins when heated with zinc dust and methanol.



$$\begin{matrix} CH_2Br \\ | \\ CH_2Br \end{matrix} \text{ or } \begin{matrix} CH_3 \\ | \\ CHBr_2 \end{matrix} + Zn \rightarrow \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + ZnBr_2$$

Polymethylene dihalides in which the two halogen atoms are in 1,3 to 1,6 position give cycloalkanes, *e.g.*, tetramethylene bromide gives cyclobutane with zinc dust and methanol.



$$\begin{matrix} CH_2{-}CH_2Br \\ | \\ CH_2{-}CH_2Br \end{matrix} + Zn \longrightarrow \begin{matrix} CH_2{-}CH_2 \\ |\quad\ \ | \\ CH_2{-}CH_2 \end{matrix} + ZnBr_2$$

Cyclobutane

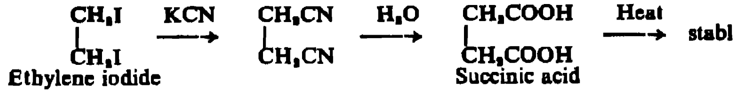
---

*Two or more hydroxyl groups when attached to the same carbon atom are generally found to be unstable and readily eliminate a molecule of water.

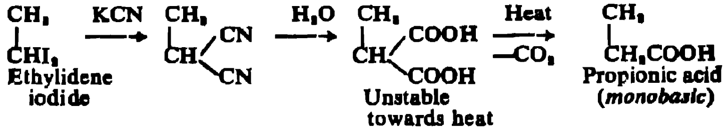
(*iv*) Alkylene iodides tend to eliminate iodine particularly at raised temperatures to form olefins, *e.g.*,

$$\underset{\text{Propylene iodide}}{CH_3.CHI.CH_2I} \xrightarrow{\text{Heat}} \underset{\text{Propylene}}{CH_3.CH{=}CH_2} + I_2$$

(*v*) *Reaction with potassium cyanide followed by hydrolysis and heating.* Alkylene halides produce dibasic acids while alkylidene halides yield monobasic acids.



$$\underset{\text{Ethylene iodide}}{\begin{matrix}CH_2I\\|\\CH_2I\end{matrix}} \xrightarrow{KCN} \begin{matrix}CH_2CN\\|\\CH_2CN\end{matrix} \xrightarrow{H_2O} \underset{\text{Succinic acid}}{\begin{matrix}CH_2COOH\\|\\CH_2COOH\end{matrix}} \xrightarrow{\text{Heat}} \text{stable}$$



Reactions (*i*) and (*v*) can be used to distinguish between the two classes of dihalides.

INDIVIDUAL MEMBERS

14. **Methylene Chloride, CH_2Cl_2.**—It was formerly manufactured by partial reduction of chloroform with zinc and hydrochloric acid in alcoholic solution.

$$CHCl_3+2[H] \longrightarrow CH_2Cl_2+HCl$$

It is now manufactured by direct chlorination of methane also (*see* methyl chloride page 2·99). It is a liquid (b.p. 313K) and is used as an industrial solvent.

15. **Ethylene Chloride, $CH_2Cl.CH_2Cl$** (b.p. 357K) **and Ethylidene chloride, CH_3CHCl_2** (b.p. 330K).—These are isomers. The former is prepared by the action of chlorine on ethylene and the latter by treating acetaldehyde with phosphorus pentachloride or by the action of hydrogen chloride on acetylene.

The two can be distinguished by hydrolysis with aqueous alkali when ethylene chloride gives glycol and ethylidene chloride gives acetaldehyde.

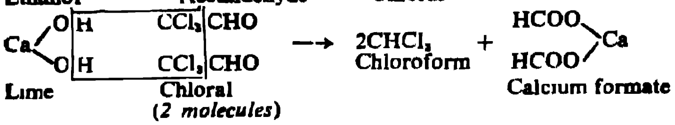
TRIHALOGEN DERIVATIVES

16. **Trihalogen Derivatives.**—The trihalogen derivatives are obtained by replacement of three hydrogen atoms of a paraffin by three halogen atoms. The most important trihalogen derivatives are those of methane and are commonly known by their trivial names : chloroform, $CHCl_3$, bromoform, $CHBr_3$ and iodoform, CHI_3. Of these chloroform and iodoform will be discussed here.

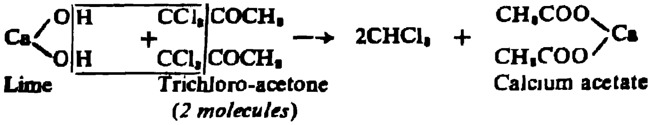
17. **Chloroform, Trichloromethane, $CHCl_3$.**—

Preparation. (1) Chloroform is **prepared in the laboratory or industrially** *by the action of bleaching powder or chlorine and alkali on ethanol or acetone.* The yield is about 40 per cent but the reaction is extremely complicated and the mechanism is obscure. Probably available chlorine in bleaching powder first oxidises ethanol to acetaldehyde which is then chlorinated to trichloro-acetaldehyde or chloral. Chloral reacts with free lime (present in bleaching powder) to give chloroform and calcium formate.

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{O} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{Cl_2} \underset{\text{Chloral}}{CCl_3CHO}$$



Similarly with acetone, trichloroacetone first obtained reacts with lime to give chloroform and calcium acetate.



(2) **Chloroform is also prepared industrially :**

(*i*) *By the chlorination of methane.* (*See* under methyl chloride, page 2·99).

(*ii*) *By the partial reduction of carbon tetrachloride with iron filings and water.*

$$\underset{\text{Carbon tetrachloride}}{CCl_4} + 2[H] \rightarrow \underset{\text{Chloroform}}{CHCl_3} + HCl$$

Chloroform manufactured by these methods is used for solvent purposes as it is not of the purity needed for its use as an anaesthetic.

(3) **Pure chloroform** may be prepared by distilling chloral hydrate with the concentrated aqueous solution of caustic soda or caustic potash.

$$\underset{\text{Chloral hydrate}}{CCl_3\overset{H|ONa}{CH(OH)_2}} + NaOH \rightarrow \underset{\text{Chloroform}}{CHCl_3} + \underset{\text{Sod. formate}}{HCOONa} + H_2O$$

18. Properties of Chloroform.—

Physical. Chloroform is a colourless, mobile liquid (b.p. 333K) with sweet sickly odour and taste. It is sparingly soluble in water, but readily soluble in ether. Chloroform itself is a solvent for oils, fats, waxes and resins Its vapours cause unconsciousness. Under usual conditions, chloroform does not burn in air, but its vapours may be ignited when it burns with a green-edged flame.

Chemical : (*i*) **Oxidation.** In the presence of air and sunlight it is slowly oxidised to carbonyl chloride or phosgene (*dangerously poisonous*).

$$\underset{\text{Chloroform}}{2CHCl_3} + O_2 \xrightarrow{\text{Air and light}} \underset{\text{Phosgene}}{2COCl_2} + 2HCl$$

$$4CHCl_3 + 3O_2 \xrightarrow{\text{Excess oxygen}} 4COCl_2 + 2Cl_2 + 2H_2O$$

(*ii*) **Reduction.** Chloroform on reduction with zinc and hydrogen chloride in ethanolic solution (acidic medium) gives methylene chloride, CH_2Cl_2. Methane is obtained on reduction of chloroform with zinc and water (neutral medium).

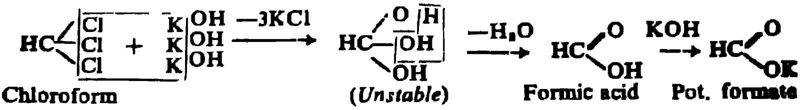
$$CHCl_3 \xrightarrow[\text{in } C_2H_5OH]{Zn/HCl} CH_2Cl_2$$

$$CHCl_3 \xrightarrow{Zn/H_2O} CH_4$$

(*iii*) **Chlorination.** On further chlorination it yields carbon tetrachloride, CCl_4.

$$CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$$

(*iv*) **Hydrolysis.** When boiled with concentrated aqueous or ethanolic alkali, chloroform is hydrolysed to formic acid.



or $$CHCl_3 + 4KOH \xrightarrow{H_2O} 3KCl + HCOOK + 2H_2O$$

The mechanism proposed for hydrolysis involves the intermediate formation of dichloromethylene, : CCl_2.

$$CHCl_3 + OH^- \rightleftharpoons :CCl_3^- + H_2O$$

$$:CCl_3^- \rightarrow :CCl_2 + Cl^-$$

$$:CCl_2 \xrightarrow[H_2O]{OH^-} HCOO^- + 2Cl^-$$

(*v*) **Nitration.** When treated with concentrated nitric acid, chloroform gives *chloropicrin*, a liquid (b.p. 385K) used as an insecticide and war gas.

$$\underset{\text{Chloroform}}{Cl_3C|H} + \underset{\text{Nitric acid}}{HO|NO_2} \longrightarrow \underset{\text{Chloropicrin}}{Cl_3C.NO_2} + H_2O$$

(*vi*) **Carbylamine reaction.** With a primary amine and alcoholic potash, chloroform gives an offensive smell of carbylamine.

$$\underset{\text{Aniline}}{C_6H_5N|H_2} + \underset{\text{Chloroform}}{Cl_3H|C} + \underset{(\textit{Alcoholic})}{3KOH} \longrightarrow \underset{\text{Phenyl isocyanide}}{C_6H_5NC} + 3KCl + 3H_2O$$

It has been suggested that the reaction proceeds via the intermediate formation of dichloromethylene (see under hydrolysis).

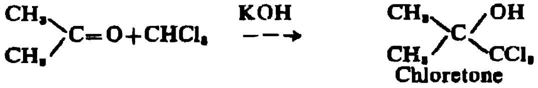
$$R\ \overset{\curvearrowright}{\ddot{N}H_2} + :CCl_2 \longrightarrow R\ \overset{+}{N}H_2-\overset{-}{C}Cl_2 \xrightarrow{-H^+}$$

$$R\ \ddot{N}\ H-\overset{-}{C}Cl_2 \xrightarrow[-H^+]{-Cl^-} R\ \ddot{N}=\overset{-}{C}Cl \xrightarrow{-Cl^-} RN \stackrel{\rightarrow}{=} C$$

(*vii*) **Heating with silver powder.** Acetylene is obtained when chloroform is warmed with silver powder.

$$\underset{\text{Chloroform}}{2CHCl_3} + 6Ag \longrightarrow \underset{\text{Acetylene}}{CH \equiv CH} + 6AgCl$$

(*viii*) **With acetone.** In the presence of potassium hydroxide chloroform adds on to the carbonyl group of ketones, *e.g.*, with acetone it gives chloretone (colourless needle-shaped crystals—m.p. 370K) used in medicine.



19. **Tests.**—The following properties of chloroform can be used as tests :

(*i*) Characteristic sweet sickly odour.

(*ii*) *Carbylamine reaction,* as given above, serves as a delicate test for chloroform.

(*iii*) Pure chloroform does not give any precipitate with silver nitrate. Thus purity of chloroform needed for anaesthetic purposes is tested with silver nitrate.

20. **Uses.**—Chloroform finds use :

(*i*) As an anaesthetic.

(*ii*) As industrial solvent for fats, waxes, resins, rubber, etc.

(*iii*) As laboratory reagent and in medicine.

(*iv*) As preservative for anatomical specimens.

(*v*) As a flavouring agent.

21. **Chloroform as an Anaesthetic.**—Chloroform is extensively employed in surgery as an anaesthetic. Its anaesthetic power was discovered and applied by Simpson in 1847. Owing to its bad effect on the heart, chloroform is being replaced by better anaesthetics such as ether, ethylene and ethylene chloride. Anaesthetic chloroform must possess a high degree of purity. In the presence of air and light, chloroform slowly forms phosgene which is extremely poisonous.

$$2CHCl_3+O_2 \xrightarrow{\text{Air and light}} 2COCl_2+2HCl$$

Precautions are, therefore, taken in storage of chloroform needed for hospital use. For example,

(*i*) It is stored in dark-brown or blue bottles kept in dark rooms.

(*ii*) The bottles are filled up to brim and well stoppered to exclude air.

(*iii*) About 1% of ethanol is added but its function is not quite clear. According to some authors it retards oxidation while others believe it combines with phsogene to give non-toxic ethyl carbonate.

$$\underset{\text{Phosgene}}{COCl_2} + \underset{\text{Ethanol}}{2C_2H_5OH} \longrightarrow \underset{\text{Ethyl carbonate}}{CO(OC_2H_5)_2} + 2HCl$$

22. Iodoform, Tri-iodomethane, CHI_3.—

Preparation. (*i*) **Laboratory Method.** Iodoform is prepared in the laboratory by the action of iodine on sodium carbonate solution containing ethanol or acetone.

(1) *With ethanol* :

$$\underset{\text{Ethanol}}{C_2H_5OH}+4I_2+3Na_2CO_3 \longrightarrow \underset{\text{Iodoform}}{CHI_3}+5NaI+\underset{\text{Sod. formate}}{HCOONa}+3CO_2+2H_2O$$

(2) *With acetone* :

$$\underset{\text{Acetone}}{CH_3.CO.CH_3}+3I_2+2Na_2CO_3 \longrightarrow \underset{\text{Iodoform}}{CHI_3}+3NaI+\underset{\text{Sod. acetate}}{CH_3COONa}+2CO_2+H_2O$$

Mechanism of the reaction is not exactly known. It is probably similar to that of the preparation of chloroform.

Expt. To a solution of 10 g sodium carbonate in 50 ml of water in a dish is added 5 ml of ethanol. This is warmed to 333K on a water bath and 5 g of iodine is gradually added till a permanent reddish tinge is obtained. A few drops of caustic soda are added to discharge the colour. Yellow crystals of iodoform separate. These are filtered, washed with water and recrystallized from alcohol.

(*ii*) **Manufacture.** It is prepared on an industrial scale by electrolysis of an aqueous solution of ethanol or acetone containing sodium carbonate and sodium or potassium iodide. Ethanol gives a better yield of iodoform than acetone. The solution is maintained at 333-343K and a current of carbon dioxide is passed in to neutralize the sodium hydroxide produced as a result of electrolysis. Iodine and sodium carbonate obtained during electrolysis react with ethanol or acetone as given above to give iodoform.

Properties of Iodoform.

Physical. It is a pale-yellow solid which crystallizes in hexagonal plates (m.p. 388K) with characteristic unpleasant odour. It is insoluble in water but readily soluble in ethanol and ether. Iodoform is used as an antiseptic but its antiseptic properties are due to liberation of free iodine and not to iodoform itself.

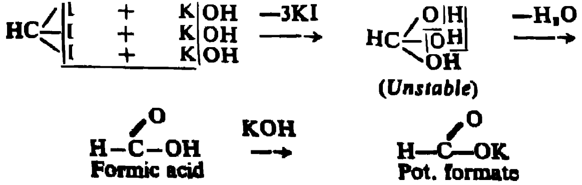
Chemical. Iodoform resembles chloroform in its chemical behaviour but it is less stable than the latter. For example,

(*i*) **Stability.** On heating iodoform decomposes to give iodine vapour. Similarly moisture, air and light liberate free iodine.

(*ii*) **Reduction.** Iodoform on reduction with phosphorus and hydriodic acid yields methylene iodide, CH_2I_2.

$$CHI_3+2[H] \rightarrow CH_2I_2+2HI$$

(*iii*) **Hydrolysis.** On boiling with alcoholic potash, iodoform gives potassium formate by hydrolysis.



(*iv*) **Carbylamine reaction.** With a primary amine and alcoholic potash, it gives an offensive smell of carbylamine (*cf.* $CHCl_3$.)

(*v*) **With silver nitrate.** Iodoform gives a yellow precipitate of silver iodide when heated with *silver nitrate*, showing its instability (*cf.* $CHCl_3$ which gives no such precipitate). This is due to the instability of C--I bond in comparison to C—Cl bond.

(*vi*) **Heating with silver powder.** Iodoform, when heated with silver powder, yields acetylene.

$$CH|I_3 + 6Ag + I_3|CH \longrightarrow \underset{\text{Acetylene}}{CH\equiv CH} + 6AgI$$

Uses. Iodoform is used as an antiseptic but the antiseptic action is due to the iodine that it liberates and not due to iodoform as such. Due to its objectionable smell, it has been gradually replaced by the other preparations containing iodine.

TETRAHALOGEN DERIVATIVES

23. Carbon Tetrachloride, Tetrachloromethane, CCl_4.—

Preparation. Carbon tetrachloride is prepared industrially :

(*i*) *By the action of chlorine on carbon disulphide in the presence of aluminium chloride as a catalyst.*

$$\underset{\substack{\text{Carbon}\\\text{disulphide}}}{CS_2} + 3Cl_2 \xrightarrow{AlCl_3} \underset{\substack{\text{Carbon}\\\text{tetrachloride}}}{CCl_4} + \underset{\substack{\text{Sulphur}\\\text{monochloride}}}{S_2Cl_2}$$

Carbon tetrachloride is freed from sulphur monochloride by fractional distillation. It is then washed with sodium hydroxide solution and distilled.

(*ii*) *By the chlorination of methane* (*see under methyl chloride*).

$$CH_4 + 4Cl_2 \rightarrow CCl_4 + 4HCl$$

Properties of Carbon Tetrachloride.

Physical. Carbon tetrachloride is a colourless heavy liquid (b.p. 350K) with a sickly odour. It is insoluble in water but readily soluble in ethanol and ether. Its vapours being non-inflammable, carbon tetrachloride is extensively used as an industrial solvent for fats, oils, resins, lacquers, etc., and as a fire extinguisher under the name *Pyrene.*

Chemical. (*i*) **Stability.** Carbon tetrachloride is stable at red heat (775K) but when its vapours come in contact with water vapour at this temperature some phosgene is formed.

$$CCl_4 + H_2O \longrightarrow COCl_2 + 2HCl$$

Hence precautions should be taken while using pyrene as fire extinguisher. The room should be well ventilated after the fire is extinguished.

(*ii*) **Reduction.** Carbon tetrachloride gives chloroform when reduced with moist iron filings.

$$CCl_4 + 2[H] \longrightarrow CHCl_3 + HCl$$

(*iii*) **Hydrolysis.** It is hydrolysed with hot ethanolic alkali to give potassium chloride and potassium carbonate.

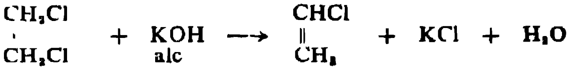
$$CCl_4 \xrightarrow[-4KCl]{+4KOH} C(OH)_4 \xrightarrow{-2H_2O} CO_2 \xrightarrow{KOH} K_2CO_3$$

Uses. (i) Industrial solvent.
(ii) In dry-cleaning.
(iii) As a fire existinguisher under the name *Pyrene.*

UNSATURATED HALOGEN COMPOUNDS

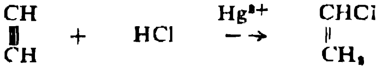
24. Vinyl Chloride, Chloroethene, $CH_2=CHCl$.—

Preparation. (i) *Vinyl chloride is conveniently prepared in the laboratory by the action of dilute ethanolic potash on ethylene chloride.*

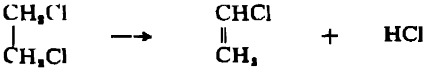

$$\begin{array}{c}CH_2Cl\\|\\CH_2Cl\end{array} + \underset{alc}{KOH} \longrightarrow \begin{array}{c}CHCl\\\|\\CH_2\end{array} + KCl + H_2O$$

(ii) It can be manufactured—

(a) *By passing acetylene into dilute hydrochloric acid at 340K in the presence of Hg^{2+} ions (catalyst).*


$$\begin{array}{c}CH\\|||\\CH\end{array} + HCl \xrightarrow{Hg^{2+}} \begin{array}{c}CHCl\\\|\\CH_2\end{array}$$

(b) *By thermal decomposition of ethylene chloride at 870-920K.*


$$\begin{array}{c}CH_2Cl\\|\\CH_2Cl\end{array} \longrightarrow \begin{array}{c}CHCl\\\|\\CH_2\end{array} + HCl$$

Properties and Uses. It is a colourless gas which liquefies at −261K.

The halogen atom in vinyl chloride is not reactive. Thus it does not undergo the usual double decomposition reactions of the alkyl halides and does not form Grignard reagent.

The non-reactivity of the chlorine atom in vinyl chloride may be explained as follows :

If the chlorine atom has sp^2 hybridisation, the C—Cl bond will be a σ-bond and the two lone pairs of electrons will occupy the other two sp^2 hybrid orbitals. This would leave a p-orbital containing a lone pair, and this orbital could now conjugate with π bond of the ethylenic linkage (Fig. 17·1).

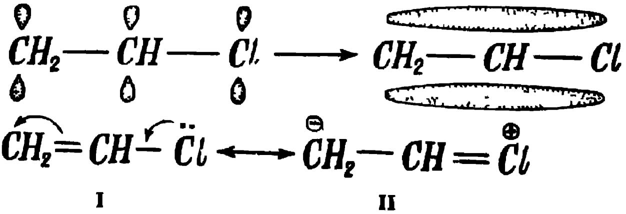


Fig. 17 1

Owing to delocalisation of bonds (through conjugation), vinyl chloride molecule has an increased stability. Before the chlorine atom can be displaced by some other groups, the lone pair must be localised again on the chlorine atom. This requires energy and so the chlorine is more firmly bound than had no conjugation occurred.

In terms of Valency Bond Approach vinyl chloride is a resonance hybrid of two structures **I** and **II** (Fig. 17·1). In **II** chlorine is joined to carbon by a double bond and bears a positive charge while carbon of CH_2 group carries a negative charge. Vinyl chloride is, therefore, stabilised due to resonance. The low reactivity of vinyl chloride towards nucleophilic substitution is due to the following factors :

(*i*) Carbon-chlorine bond has some double bond character and is, therefore, stronger than a pure single bond.

(*ii*) Carbon atom is *sp*²-hybridised and the bond to chlorine is shorter (=1·69Å) and stronger than in alkyl halides (C—Cl length =1·77-1·80Å) where carbon is *sp*³-hybridised. The vinyl halide molecule is, therefore, more stable.

(*iii*) Vinyl chloride is resonance stabilised. This stabilisation creases the E_{act} for displacement and thus slows down the reaction.

It, however, gives the usual addition reactions of the double bond, *e.g.*, it gives addition compounds with halogens and halogen acids.

During electrophilic addition of H^+ to an olefin and $CH_2{=}CHCl$ a carbocation is obtained. Just as electron release by alkyl groups disperses the positive charge and stabilises a carbocation (the order of stability being 3°>2°>1°), an electron withdrawal by chlorine intensifies the positive charge and destabilises the carbocation, $\overset{\oplus}{C}H_3{-}CH_2Cl$. Vinyl chloride is, therefore, less reactive as compared to ethylene.

Vinyl halide being very unreactive can be dehydrohalogenated only under vigorous conditions—use of a stronger base.

$$CH_2{=}CHCl \xrightarrow[-HCl]{NaNH_2} HC{\equiv}CH$$

It is used in the manufacture of plastics.

25. Allyl Halides, 3-Halogenopropene, $CH_2{=}CH.CH_2X$.—

Allyl Chloride, $CH_2{=}CH.CH_2Cl$. (b.p. 328K). It is prepared industrially by chlorination of propene at high temperature (*see* Alkenes). In the laboratory it may be prepared by warming allyl alcohol with hydrochloric acid.

$$CH_2{=}CH.CH_2OH+HCl \rightarrow CH_2{=}CH.CH_2Cl+H_2O$$

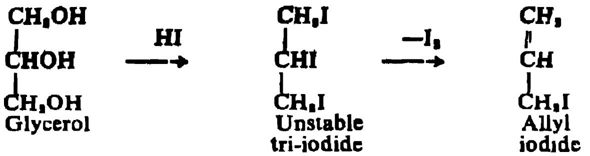
The reactivity of allyl alcohol is more characteristic of a tertiary alcohol than a primary alcohol. This may be explained by an S_N1 mechanism operating because of the stability of allyl cation as explained on the next page.

Allyl bromide, $CH_2{=}CH.CH_2Br$ (b.p. 343K). It is prepared in the laboratory by distilling allyl alcohol with 48% HBr in presence of sulphuric acid.

$$CH_2{=}CH.CH_2OH+HBr \longrightarrow CH_2{=}CH.CH_2Br+H_2O$$

Allyl Iodide, 3-Iodo-1-propene, $CH_2{=}CH.CH_2I$.

Preparation. Allyl iodide may be prepared by heating glycerol with small amount of hydriodic acid.



$$\underset{\text{Glycerol}}{\begin{array}{l}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{array}} \xrightarrow{HI} \underset{\substack{\text{Unstable}\\ \text{tri-iodide}}}{\begin{array}{l}CH_2I\\ |\\ CHI\\ |\\ CH_2I\end{array}} \xrightarrow{-I_2} \underset{\substack{\text{Allyl}\\ \text{iodide}}}{\begin{array}{l}CH_2\\ \|\\ CH\\ |\\ CH_2I\end{array}}$$

Properties and Uses. It is a colourless liquid (b.p. 373·1K) having a garlic odour.

The halogen atom in allyl halides is more reactive than in alkyl halides. So it gives the usual replacement reactions, *e.g.*,

$$\underset{\text{Allyl iodide}}{CH_2{=}CH.CH_2I} + \underset{(aqueous)}{KOH} \longrightarrow \underset{\text{Allyl alcohol}}{CH_2{=}CH.CH_2OH} + KI$$

Properties of allyl chloride are similar to those of allyl iodide and the chlorine atom in allyl chloride is highly reactive. The usual reactivity of the halogen atom may be explained as follows :

If chlorine were to ionise the carbon atom to which it was attached now has a positive charge and has only *six* electrons. Hence the π-bond covering the other two carbon atoms can extend to embrace this third carbon atom by delocalisation of electrons. The net result is a molecular orbital covering *three* carbon atoms and so the delocalisation energy will be increased, *i.e.*, the new arrangement is stabilised and behaves as if the chlorine atom is ionic (Fig. 17·2)

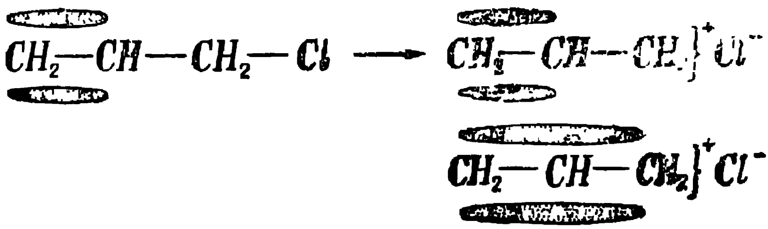


Fig. 17·2.

In terms of the valency bond approach, the reactivity of chlorine atom is due to its ionization. The reason for the ease of ionization is the considerable stabilisation of the carbocation due to its forming a resonance hybrid.

$$CH_2{=}CH{-}CH_2Cl \longrightarrow [CH_2{=}CH{-}{-}\overset{+}{C}H_2 \longleftrightarrow \overset{+}{C}H_2{-}CH{=}CH_2] + Cl^-$$

The allyl halides add on halogen acids to give a mixture of the 1, 2- and 1, 3- dihalides. Addition of HBr to allyl bromide has been studied in detail.

$$CH_2{=}CH.CH_2Br + HBr \longrightarrow \underset{\text{1, 3-dibromide}}{CH_2Br.CH_2.CH_2Br} + \underset{\text{1, 2-dibromide}}{CH_3.CHBr.CH_2Br}$$

In the presence of peroxides 1,3-dibromide is obtained in 90% yield whereas in absence of peroxides 1,2-dibromide is obtained in 90% yield.

It is suggested that 1, 3-dibromide is formed by a free-radical mechanism whereas mechanism for the formation of 1, 2-dibromide is polar. This can be explained in terms of hyperconjugation (*see page 1·101*).

26. *Some Commercially known Halogen Derivatives.*

(*i*) **Westron or Acetylene tetrachloride.** It is prepared by passing a mixture of acetylene and chlorine into chambers containing iron filings and kieselguhr.

$$CH{\equiv}CH+2Cl_2 \longrightarrow \underset{\text{Westron}}{CHCl_2{-}CHCl_2}$$

It is a colourless, non-inflammable heavy liquid (b.p. 419K) used commercially as a solvent for oils, paints, varnishes, rubber, etc.

(*ii*) **Westrosol or Trichloroethylene.** It is prepared by passing westron over heated barium chloride (*catalyst*)

$$\underset{\text{Westron}}{CHCl_2{-}CHCl_2} \xrightarrow{BaCl_2} \underset{\text{Westrosol}}{CHCl{=}CCl_2} + HCl$$

It is a colourless, non-inflammable liquid (b.p. 361-363K), smelling like chloroform. It is less toxic, more stable and better industrial solvent than westron.

(*iii*) **Freon or Dichlorodifluoromethane, CCl_2F_2.** Freon is prepared by the action of antimony fluoride on carbon tetrachloride in the presence of antimony pentachloride (*catalyst*).

$$3CCl_4+2SbF_3 \xrightarrow{SbCl_5} \underset{\text{Freon}}{3CCl_2F_2}+2SbCl_3$$

It is a colourless, non-toxic and non-inflammable gas (b.p. 244K) widely used in electrical refrigerators and air-conditioning plants.

27. Kinetics of Nucleophilic Aliphatic Substitution.— Hydrolysis of alkyl halides yields alcohols.

$$HO^-+R{-}X \rightarrow HO{-}R+X^-$$

Investigation of the kinetics of such reactions has shown that these are essentially of two types :

(*i*) Those in which rate of reaction is given by the relation :

$$\text{Rate} \propto [RX][OH^-] \qquad ...(1)$$

These are termed Second order reactions or Bimolecular reactions.

(*ii*) Those in which rate of reaction is independent of $[OH^-]$, *i.e.*,

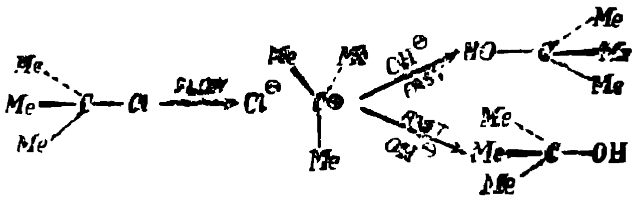
$$\text{Rate} \propto [RX] \qquad ...(2)$$

These are termed First order reactions or Unimolecular reactions.

In many cases the kinetics are mixed, *i.e.*, these reactions show both types of rate laws simultaneously.

Relation of Kinetics to Mechanism. It was found that hydrolysis of methyl bromide by aqueous alkali is a second order reaction, *i.e.*, it proceeds according to Eqn. (1) and both CH_3Br and OH^- participate in the rate determining step (*rds*). Mechanism of this reaction involving the formation of a transition state as intermediate has been discussed at length on page 1·151. It is accompanied by inversion of configuration termed ***Walden Inversion***. **This is termed S_N2 mechanism standing for Substitution Nucleophilic bimolecular.**

On the other hand hydrolysis of *tert*-butyl chloride with aqueous alkali has been found to be first order reaction following Eqn. (2) kinetically, *i.e.*, the rate is independent of [OH^-]. In other words, [OH^-] does not play any part in the *rds*. The following mechanism has been suggested for this.

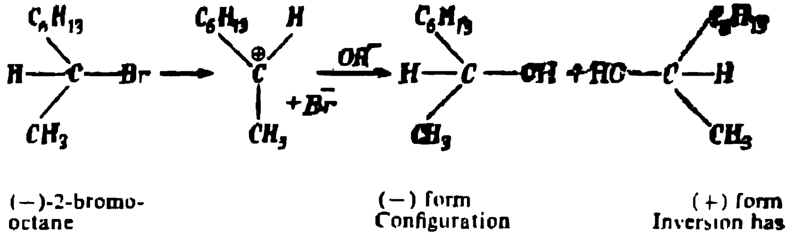


This type of mechnism is termed S_N1 standing for Substitution Nucleophilic unimolecular.

The energy needed for ionisation is largely supplied by energy released during solvation of ions produced. The carbocation formed has a planar state in which three methyl groups are as far apart as possible. Attack by the nucleophile OH^- mav be from either side. The product may or may not be accompanied by inversion of configuration

During hydrolysis of an optically active alkyl halide, since the nucleophile can attack either face of the carbocation formed as intermediate product two enantiomers will be obtained, probably in equal amounts. As such the product obtained should be a racemic mixture. However, in actual practice racemisation does not take place.

It is suggested that the nucleophilic species attack the carbocation even before the leaving group (X^-) has moved sufficiently awav. As such the nucleophile attacks only from the back side, the front side being shielded by the departing halide ion. As a result of it, product with inverted configuration obtained by the nucleophilic attack from the back side predominates. In other words, the product obtained is only partially racemised. This view has been confirmed by the partially racemised product obtained by hydrolysis of (—)2-bromooctane with dilute alkali

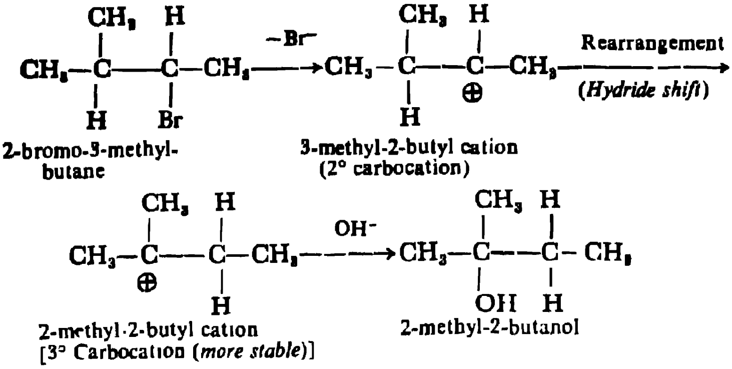


(—)-2-bromo-octane

(—) form Configuration retained (Less favourable)

(+) form Inversion has taken place (More favourable)

Rearrangements in S_N1 Reactions. Since S_N1 reactions involve the formation of a carbocation as an intermediate, the carbocation may undergo rearrangement to form a more stable carbocation. The final product in such cases will be different from the expected one. For example, 2-bromo-3-methylbutane on hydrolysis gives 2-methyl-2-butanol.



No such rearrangement occurs in S_N2 reactions since these do not involve intermediate carbocations.

Reactivities of Alkyl Halides in S_N1 and S_N2 Reactions. As explained on page 1 148 relative reactivities of alkyl halides involved in S_N1 reactions, based on the stabilities of carbocations formed by them are :

Benzyl halides, Allyl halides>Tertiary halides>Secondary halides>Primary halides>Methyl halides.

Reactivities of alkyl halides in S_N2 substitution is governed by steric factors—the bulkier the group, less reactive it is. Methyl halides>Primary halides>Secondary halides>Tertiary halides.

Factors influencing Mechanism. We have learnt that in general primary alkyl halides follow S_N2 mechanism whereas tertiary alkyl halides react by S_N1 mechanism. Secondary alkyl halides may sometimes undergo both but except in very polar solvents, S_N2 predominates. In addition to the nature of the alkyl halides (**Subtrates**) various other factors which influence the mechanism of nucleophilic substitution are :

(*i*) **Nature of alkyl groups in the alkyl halide.** Bulkier R groups favour S_N1 over S_N2. Since it is difficult for the nucleophile to get to the reactive $C^{\delta+}$, the alkyl halide is more likely to ionize before S_N2 attack can take place.

(*ii*) **Nature of the nucleophilic reagent.** Strong nucleophilic reagents (*e.g.*, OH^- and ^-OR) favour S_N2 mechanism as these are powerful enough to push out the halide ion. Weak nucleophilic reagents (*e.g.*, H_2O, ROH) favour S_N1 mechanism since these can attack the carbocation already formed, with comparative ease.

(*iii*) **Concentration of nucleophilic reagent.** Higher concentrations favour S_N2 mechanism whereas lower concentrations favour S_N1 mechanism.

(*iv*) **Nature of Solvent.** Polar and protic solvents favour S_N1 mechanism since these help ionisation of alkyl halide by solvating R^+ and X^- ions. Protic solvents (those capable of furnishing hydrogen ions, H^+ for hydrogen bonding) are very good at solvating X^- ions.

In the case of S_N2 mechanism the transition state is less polar than the reactants. Polar solvent can solvate the reactants more effectively than the transition state. As such, polar solvents slow down slightly the rate of the S_N2 reaction.

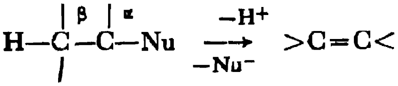
In short, polar solvents favour S_N1 mechanism whereas non-polar solvents favour S_N2 mechanism.

(*v*) **The use of electrophilic catalysts.** Lewis acids such as H^+, Ag^+, Hg^{2+}, $ZnCl_2$ and $AlCl_3$ favour S_N1 over S_N2 because these catalysts accept electrons from the leaving group ($:X^-$) and thus provide some sort of electrophilic pull which helps ionization $R-X$.

Comparative Survey of S_N1 and S_N2 Reactions. Distinguishing features of the two mechanisms are summarised below :

	S_N1 reactions	S_N2 reactions
1.	These are first order reactions.	These are second order reactions.
2.	The nucleophile can attack from the back side as well as from the front side, although the former predominates.	The nucleophile can attack only from the back side.
3.	Partial racemisation occurs in case of optically active alkyl halides.	Walden inversion takes place.
4.	Reaction rate determined solely by electronic factors.	Reaction rate determined by steric factors.
5.	The order of activities of alkyl halides is : Benzyl, allyl $>3^\circ>2^\circ>1^\circ>CH_3X$	The order of activities is : $CH_3X>1^\circ>2^\circ>3^\circ$ halides
6.	Favoured by the presence of bulkier alkyl group in RX	Favoured by the presence of fewer and simpler R groups.
7.	Rearrangement is possible.	Rearrangement is not possible.
8.	Favoured by mild nucleophilic reagents.	Favoured by strong nucleophilic reagents.
9.	Favoured by lower concentrations of the nucleophilic reagents.	Favoured by higher concentrations of the nucleophilic reagents.
10.	Favoured by polar solvents.	Favoured by non-polar solvents or those of low polarity.
11.	Favoured by the presence of electrophilic catalysts.	Favoured by absence of electrophilic catalysts.

28. Kinetics of Elimination Reactions.—Reactions involving removal of two groups from a molecule without being replaced by other groups are termed *Elimination reactions.* In majority of these reactions the two groups are lost from adjacent carbon atoms. One of the groups eliminated is generally a proton and the other a nucleophile, resulting in the formation of a multiple bond.



$$\text{H—}\overset{|\,\beta}{\underset{|}{\text{C}}}\text{—}\overset{|\,\alpha}{\text{C}}\text{—Nu} \xrightarrow[-\text{Nu}^-]{-\text{H}^+} >\text{C}=\text{C}<$$

Some familiar examples of elimination reactions are

(*i*) *Base-induced dehydrohalogenation of alkyl halides.*

$$RCH_2.CH_2X \xrightarrow{^-OH} RCH=CH_2+H_2O+X^-$$

(*ii*) *Acid-catalysed dehydration of alcohols.*

$$RCH_2.CH_2OH \xrightarrow{H^+} RCH=CH_2+H_3O^+$$

The carbon atom losing Nu^- is termed α-carbon atom and the other losing a proton is referred to as the β-carbon. The overall process of elimination is known as **β-elimination**.

Elimination reactions take place either by a unimolecular (E1) mechanism or a bimolecular (E2) mechanism. These have been discussed in detail on page 1·153.

E2 eliminations are stereospecific *trans* eliminations. In such eliminations it is considered necessary that the attacking atom of the base, hydrogen to be eliminated as proton, the two carbon atoms (C_α , C_β) and the leaving group should all be coplanar in the intermediate transition state (*see page* 1·155).

Factors favouring E1 over E2.

(*i*) *Presence of alkyl groups on the α-C or β C of the alkyl halides.* Presence of these groups stabilises the E1 carbocation intermediate. Thus the order of ease of E1 elimination is :

$$3^\circ > 2^\circ > 1^\circ$$

In fact only tertiary alkyl halides give extensive E1 elimination.

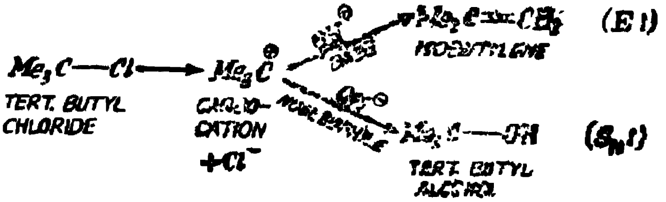
(*ii*) *Good leaving groups.* The better the leaving group, the more likelihood of E1 elimination. The halides arranged in the order of decreasing leaving ability are :

$$—I > —Br > —Cl > —F$$

(*iii*) *Weak. Dilute bases.* Strong, concentrated bases tend to attack a β-H atom giving E2 elimination before E1 ionization can take place to give carbocation intermediate.

(*iv*) *Polar solvents.* Polar solvents can solvate the ions more strongly and thus stabilise them. Thus they encourage E1 ionization.

29. Elimination *vs.* Substitution.—In both E1 and S_N1 reactions of an alkyl halide with OH^- the intermediate step is the formation of a carbocation which is then attacked rapidly by OH^-. **In E1 reaction OH^- acts as a base** (*electron pair donor towards hydrogen*) *and abstracts a proton* from a β-carbon atom to yield an alkene. **In S_N1 reactions OH^- acts as a nucleophile** *(an electron pair donor towards carbon)* and the overall result is the formation of a substitution product.



Conditions which favour S_N1 reactions will lead to E1 reactions also. The ratio of the two products obtained has been found to be fairly constant for a given alkyl group, no matter which halogen atom is lost.

Branching at the β-carbon atom tends to favour E1-elimination, the reason being partly steric. The more branched the alkyl halide, the more crowding is released during the formation of carbocation intermediate. During S_N1 reaction crowding is reintroduced with the energy of the nucleophile. Hence substitution is less favoured. By contrast loss of a proton during E1 reaction results in further relief of strain. Hence elimination is preferred more. Hyperconjugation which stabilises an alkene also favours E1 reaction.

Elimination has normally higher activation energy and is, therefore, favoured at higher temperature.

In bimolecular reactions also *increasing alkyl substitution favours elimination at the expense of substitution*. This is because S_N2 is retarded on account of the overcrowding in the transition state which leads to substitution. By contrast E2 is favoured by increasing alkyl substitution because of the hyperconjugative stabilisation of the incipient alkene in the alternative transition state leading to elimination.

Other factors which tend to favour E2 reactions over the S_N2 reactions are :

(*i*) Use of strong bases at higher concentrations.

(*ii*) Use of non-polar solvents.

(*iii*) High temperature.

We can summarize by saying that **the ratio E S_N is highest for** :

(*i*) *Nature of the alkyl halide.*

$$3° > 2° > 1°$$

(*ii*) *Strong and concentrated bases attacking alkyl halide, e.g.*,

$$NH_2^- \text{ and } OH^-$$

(*iii*) *Solvent of low polarity, e.g.*, alcoholic KOH brings about **elimination and** aqueous KOH is used for substitution.

(*iv*) ***High temperatures.***

QUESTIONS

Essay Type :

1. Describe the most important reactions of alkyl halides and illustrate with examples how they are used in synthetic chemistry.

2. (*a*) How would you prepare a pure sample of ethyl bromide in the laboratory ?

(*b*) What reagents and conditions would be used to convert ethyl bromide into (*i*) ethyl alcohol, (*ii*) ethane, (*iii*) nitromethane, and (*iv*) ethylamine ?
(*Delhi B.Sc. 1976 Supp.*)

3. (*a*) How would you obtain a pure sample of ethyl iodide in the laboratory ? How can it be converted into (*i*) propionic acid, and (*ii*) ethyl acetate ? (*Delhi B.Sc. Hons. Sub. 1976*)

(*b*) Give balanced equations for the reactions of ethyl iodide with each of the following reagents :

(*i*) Silver nitrite, (*ii*) Sodium ethoxide,
(*iii*) Sodium hydrogen sulphide, (*iv*) alcoholic ammonia.
(*Delhi B.Sc. 1976*)

(*c*) How does ethyl iodide react with KOH in (*i*) aqueous solution, (*ii*) alcoholic solution ? (*Delhi B.Sc. 1976*)

4. Describe the preparation of chloroform. What precautions must be observed in storing chloroform for use as an anaesthetic ?

What happens when chloroform is—

(*i*) oxidised in air and sunlight,
(*ii*) reduced with Zinc and HCl.
(*iii*) boiled with KOH.
(*iv*) warmed with aniline and alcoholic KOH ?
(*Delhi B.Sc. Hons. Sub. 1976 ; Jabalpur B.Sc. 1976 ; Delhi 1976*)

5. How are the following substances prepared :

(*a*) Freon, (*b*) Westrosol,
(*c*) Westron, and (*d*) Iodoform.

Give their uses.

6. Prepare the following :

(*i*) Allyl chloride from allyl alcohol and *vice versa*.
(*ii*) Ethyl iodide from ethyl chloride.
(*iii*) *n*-Butane from *sec*. butyl iodide.
(*iv*) *n*-propyl bromide from isopropyl chloride.
(*v*) Isopropyl bromide from *n*-propyl chloride.

7. How do you account for the activity or inactivity of the halogen atom in the following compounds :

(*i*) Allyl chloride. (*ii*) Vinyl chloride ?
(*Delhi B.Sc. 1976 ; B.N.C. 1977*)

8. Give the mechanism, stereochemistry and kinetics of E2 and E1 reactions in alkyl halides. (*Guru Nanak Dev B.Sc. 1977*)

9. (*a*) Alkaline hydrolysis of tertiary butyl bromide and methyl bromide are first order and second order reactions respectively. Keeping in view this fact, suggest mechanisms for these reactions along with probable transition states.

(*b*) Why do alkyl halides show nucleophilic substitution rather than electrophilic substitution ? (*G.N.D. B.Sc. 1975*)

10. Prove that hydrolysis of *tert*. butyl bromide is an S_N1 reaction.
(*B.N.C. B.Sc. 1976*)

11. Give the mechanism, stereochemistry and kinetics of S_N1 and S_N2 reactions for the hydrolysis of alkyl halides. (*G.N.D. B.Sc. 1976*)

12. Discuss in detail the mechanism of the following :

S_N1 and S_N2 reactions.

13. Discuss the kinetics of nucleophilic substitutions involving alkyl halides with special reference to : (*i*) Rate of reaction, (*ii*) S_N1 reaction mechanism, (*iii*) S_N2 reaction mechanism. (*Punjab B.Sc. 1976*)

B. Short Answer Type :

1. (*a*) Write structural formulae for :

(*i*) 2-Chloro-3-Methylbutane.
(*ii*) 1,3-Diiodo-4-octene.
(*iii*) 3-Chloro-1-iodohexane.
(*iv*) Neopentyl bromide.
(*v*) Isobutyl bromide.
(*vi*) *sec*. butyl bromide.
(*vii*) [illegible]-Dibromopentane.

2. Name the following :

(*i*) $(CH_3)_3.CBr$.
(*ii*) $(CH_3)_2CCl_2$.
(*iii*) $CH_3.CHBr.CH_2Br$.
(*iv*) $CH_2Br.CH_2.CH_2Br$.

3. How do you explain the high reactivity of alkyl halides ? (*Delhi B.Sc. 1977*)

4.. The reactivity order of the following compounds is as follows :

Tertiary alkyl bromide > Secondary alkyl bromide > Primary alkyl bromide. Explain why. (*Delhi B.Sc. 1977*)

5. How does chloroform react with the following :

(*i*) Acetone, (*ii*) Nitric acid ? (*Delhi B.Sc. 1977*)

6. Give chemical tests to distinguish between ethylene chloride and ethylidene chloride. (*Delhi B.Sc. 1976 ; B.Sc. Hons. Sub. 1977*)

7. Describe the action of aqueous KOH on (*i*) CH_3Cl, (*ii*) CH_2Cl_2, (*iii*) $CHCl_3$, (*iv*) CCl_4. Name the final product in each case. (*Delhi B.Sc. Hons. Sub. 1976*)

8. Give reactions showing how the following can be obtained from 1-bromopropane :

(*i*) propylene, (*ii*) propanol, (*iii*) nitropropane, (*iv*) butanoic acid. (*Delhi B.Sc. Hons. Sub. 1976*)

9. Give addition and substitution reactions of propane with chlorine. Name the mechanism involved. (*Delhi B.Sc. 1976*)

10. Explain briefly why chlorine atom in vinyl chloride is not reactive. (*Delhi B.Sc. Hons. 1976*)

11. *t*-Butyl chloride reacts with sodium hydroxide solution by S_N1 mechanism while *n*-butyl chloride reacts by the S_N2 mechanism. Explain, why ? (*Kerala B.Sc. 1975*)

12. Give one example where hydrolysis of alkyl halide proceeds according to unimolecular (S_N1) mechanism and one example where it follows bimolecular (S_N2) mechanism. (*Punjabi B.Sc. 1976 Supp.*)

13. Give suitable explanations for the following :

(*i*) 2-Butanol on dehydration gives 2-Butene
(*ii*) Propene on chlorination at 670 to 870 K gives allyl chloride.
(*iii*) Chlorine atom in vinyl chloride is not reactive.
(*iv*) *tert*-Alkyl halides usually react by S_N2 mechanism. (*Delhi B.Sc. Hons 1978*)

14. S_N1 type of reactions show racemisation and rearrangement while S_N2 type of reactions show inversion but no rearrangement. Explain. (*Delhi B. Sc. Hons. 1978*)

15.* Explain why chlorine in allyl chloride is reactive while that in vinyl chloride is not reactive. (*Andhra B. Sc. 1978*)

16. What is the order of ease of hydrolysis of the halogen in the following compounds ?

(*i*) $(CH_3)_3CCl$; (*ii*) $CH_3CH_2CHICH_3$;
(*iii*) $CH_2=CH.CH_2Br$; (*iv*) $CH_3CH_2\ CHBrCH_3$;
(*v*) CH_3CH_2CHI and (*vi*) $CH_2=CHCl$.

(*Andhra B. Sc. 1978*)

17. How do you explain the following order of reactivity ?

$$CH_3I>CH_3-Br>CH_3Cl$$

18. Why is a tertiary alkyl halide>secondary alkyl halide>primary alkyl halide ?

19. Give mechanism of isomerisation of 1-Bromobutane into 2-Bromobutane and that of neopentyl chloride into 2-Chloro-2-methylbutane when heated in the presence of $AlCl_3$ at 570 K.

20. Give equations for the conversion of glycerol into isopropyl iodide.

21. Name various factors which influence mechanism whether S_N1 or S_N2

22. Summarize distinguishing features of S_N1 and S_N2 mechanisms.

23. What is β-elimination ?

24. Why are S_N1 and E1 competing reactions ?

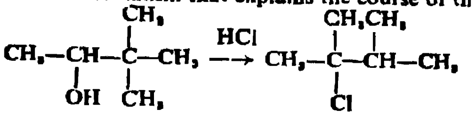
25. Why does branching at the β-carbon atom tend to favour elimination at the expense of substitution ?

26. Name the factors which tend to favour E2 reactions over the S_N2 reactions.

27. Account for the following : *t*-Butyl chloride reacts with sodium hydroxide by S_N1 mechanism while *n*-butyl chloride reacts by the S_N2 mechanism.

(*Delhi B.Sc. Hons. 1930*)

28. Write mechanism that explains the course of the following reaction :



$$CH_3-\underset{OH}{CH}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3 \xrightarrow{HCl} CH_3-\overset{CH_3}{\underset{Cl}{C}}-\overset{CH_3}{CH}-CH_3$$

(*Delhi B.Sc. Hons. 1980*)

29. When $(CH_3)_3CCl$ is treated with HO^-, the product is a mixture of isobutylene and *t*-butyl alcohol.

(*i*) Name the two types of reactions involved.

(*ii*) Name the intermediate product which gives rise to the above two products.

(*iii*) What is the function of HO^- in the two reactions ?

(*iv*) What conditions favour the formation of isobutylene ?

(*Delhi B Sc. Hons. 1980*)

30. Give electronic mechanism of the hydrolysis of methyl chloride.

(*Aligarh B.Sc. 1977 Supp.*)

31. Explain the following :

(*a*) Alkyl chlorides and allyl chloride give a precipitate of AgCl on heating with alcoholic $AgNO_3$, whereas vinyl chloride does not.

(*b*) Propylene on treatment with HBr in presence of a peroxide gives *n*-propyl bromide.

(*Delhi BSc. Hons 1981*)

32. Write equations for the following reactions. Give the mechanism in each case.

(*a*) Isoprene is treated with HBr in acetic acid.

(*b*) Isopropyl bromide is treated separately with aqueous NaOH and alcoholic NaOH.

(*c*) Equimolecular quantities of a mixture of isobutane and chlorine are exposed to sunlight.

(*Delhi B.Sc. Hons 1981*)

Problems

1. *With alcoholic potash* C_3H_7Br *(A) gives* C_3H_6 **(B) along with some** $C_6H_{14}O$ *(C) as impurity.* **B on oxidation gives** $C_2H_4O_2$ **(D)+carbon dioxide and water. With hydrobromic acid B gives E, an isomer of A. Identify the compounds A to E.**

2. A primary alkyl halide (A), C_4H_9Br reacted with alcoholic sodium hydroxide to give compound (B). Compound (B) reacted with hydrogen bromide to give (C)—an isomer of (A). When (A) was treated with sodium, it gave a compound (D), C_8H_{18} which was different from the compound produced when *n*-butyl bromide was reacted with sodium. Draw the structural formula of (A) and write equations for all reactions. *(Punjab B.Sc. Ch. Engg. 1976)*

3. With alkali $C_3H_6Cl_2$ (A) gives C_3H_6O (B) or C_3H_4 (C). C reacts with dilute sulphuric acid containing mercuric sulphate to give C_3H_6O (D) which gives with bromine in alkali, the salt of $C_2H_4O_2$ (E). Identify the compounds A to E.

ANSWERS

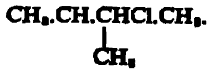
A. **6.** (*i*) $$\text{Allyl alcohol} \underset{\text{Boil with water}}{\overset{\text{Warm with HCl}}{\rightleftarrows}} \text{Allyl chloride}$$

(*ii*) With KI. (*iii*) By reduction with HI, Zn-Cu+alcohol, etc.

(*iv*) $$(CH_3)_2.CHCl \xrightarrow[\text{alc.}]{KOH} CH_3.CH{=}CH_2 \xrightarrow[+\text{Peroxide}]{HBr} CH_3.CH_2.CH_2Br$$

(*v*) $$CH_3.CH_2.CH_2Cl \xrightarrow[\text{alc.}]{KOH} CH_3.CH{=}CH_2 \xrightarrow{HBr} CH_3.CHBr.CH_3$$

B. **1.** (*i*)



$CH_3.\underset{\underset{CH_3}{|}}{CH}.CHCl.CH_3.$

(*ii*) $CH_2I.CH_2.CHI.CH{=}CH.CH_2.CH_2.CH_3.$

(*iii*) $CH_2I.CH_2.CHCl.CH_2.CH_2.CH_3.$

(*iv*) $(CH_3)_3C\ CH_2Br.$ (*v*) $(CH_3)_2CH.CH_2Br.$

(*vi*) $CH_3.CH_2.CHBr.CH_3.$ (*vii*) $CH_2Br.CH_2.CH_2.CH_2.CH_2Br.$

2. (*i*) tert.-Butyl bromide or 2-Bromo-2-Methylpropane.

(*ii*) Isopropylidene chloride or 2,2-Dichloropropane.

(*iii*) Propylene bromide or 1,2-Dibromopropane.

(*iv*) α, ω-Dibromopropane or Trimethylene bromide.

C. **1.** A is $CH_3CH_2\ CH_2Br$: *n*-Propyl bromide

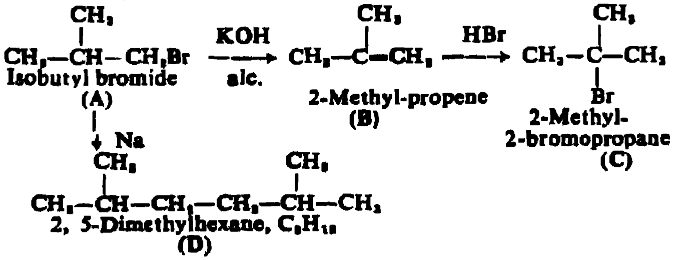
B is $CH_3CH{=}CH_2$; Propylene

C is $CH_3.CH_2.CH_2.O.CH_2.CH_2.CH_3$; *n*-Propyl ether

D is CH_3COOH ; Acetic acid

E is $CH_3.CHBr.CH_3$. Isopropyl bromide

2.



3. A is $CH_3CH_2CHCl_2$ (*Propylidene chloride*) ;

B is $CH_3.CH_2.CHO$ (*Propionaldehyde*) ;

C is $CH_3.C{\equiv}CH$ (*Propyne*) ;

D is $CH_3CO.CH_3$ (*Acetone*) ;

E is CH_3COOH (*Acetic acid*).

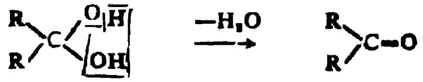
18

Monohydric Alcohols

1. The Alcohols.—The hydroxy derivatives of aliphatic hydrocarbons are termed alcohols. These are obtained by replacement of one, two or more hydrogen atoms of a hydrocarbon by a corresponding number of hydroxyl groups. They are classified according to the number of hydroxyl groups present. For example, alcohols containing one hydroxyl group are called **monohydric** while others containing two and three hydroxyl groups are termed **dihydric** and **trihydric** respectively. Alcohols containing four or more hydroxyl groups are known as **Polyhydric alcohols**. Thus, we have

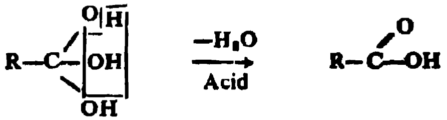
$$\begin{array}{ccc} CH_4 \ (\textit{Methane}) & CH_3{-}CH_3 \ (\textit{Ethane}) & CH_3{-}CH_2{-}CH_3 \ (\textit{Propane}) \\ -H \big\downarrow +OH & -2H \big\downarrow +2OH & -3H \big\downarrow +3OH \\ CH_3OH \ ; & CH_2OH{-}CH_2OH \ ; & CH_2OH.CHOH.CH_2OH \\ \text{Methanol} & \text{Glycol} & \text{Glycerol} \\ (\textit{Monohydric}) & (\textit{Dihydric}) & (\textit{Trihydric alcohol}) \end{array}$$

More than one —OH groups cannot be linked with the same carbon atom ; if it happens, the compound is unstable and an immediate elimination of a molecule of water occurs.



Unstable dihydric alcohol

Ketone



Unstable trihydric alcohol

2. Monohydric Alcohols.—The saturated monohydric alcohols constitute homologous series with the general formula $C_nH_{2n+1}OH$ or ROH and the characteristic group —OH. These are further classified as primary, secondary and tertiary alcohols according as the carbon atom to which the hydroxyl group is attached is primary, secondary or tertiary carbon atom.

A carbon atom is termed primary, secondary or tertiary according as it is attached to one, two or three carbon atoms respectively.

Primary alcohols contain the *primary alcoholic group*, $—CH_2OH$, *e.g.*, methanol HCH_2OH and ethanol $CH_3.CH_2OH$. Similarly $>CHOH$ is the characteristic *secondary alcoholic* group and $\equiv COH$ is the characteristic tertiary alcoholic group, *e.g.*,

$(CH_3)_2CHOH$	;	$(CH_3)_3COH$
iso-propyl alcohol		*tert*-butyl alcohol
(*Secondary alcohol*)		(*Tertiary alcohol*)

3. Nomenclature.—There are three different systems for nomenclature of monohydric alcohols as given below :

(*i*) The simpler alcohols are commonly known by their **common** or **trivial names** obtained by adding the word alcohol after the alkyl group present, *e.g.*, methyl alcohol for CH_3OH.

(*ii*) According to another system of nomenclature, alcohols are considered and named as derivatives of methyl alcohol (CH_3OH) which is named *carbinol*, *e.g.*, CH_3CH_2OH is methylcarbinol.

(*iii*) In the **IUPAC system**, the longest carbon atoms chain containing the hydroxyl group is selected as the parent alkane and the alcohol is named as derivative of this alkane with *-ol* as the class suffix. The homologous series is thus termed as *alkanols*. The positions of the hydroxyl groups and the side chains are indicated by numbers, *the lowest possible number being given to the hydroxyl group.* For example,

$$^{4}CH_3.{}^{3}\underset{\displaystyle CH_3}{\underset{|}{CH}}.{}^{2}\underset{\displaystyle OH}{\underset{|}{CH}}.{}^{1}CH_3$$

is called *3-methyl-2-butanol*.

Names of a few alcohols in these three systems are given below :

Alcohol	*Trivial name*	*Carbinol name*	*IUPAC name*
CH_3OH	Methyl alcohol	Carbinol	Methanol
$CH_3.CH_2OH$	Ethyl alcohol	Methyl carbinol	Ethanol
$CH_3CH_2CH_2OH$	*n*-propyl alcohol	Ethylcarbinol	1-propanol
$CH_3CHOH.CH_3$	Isopropyl alcohol	Dimethylcarbinol	2-propanol
$(CH_3)_2CH.CH_2OH$	Isobutyl alcohol	Isopropylcarbinol	2-Methyl-1-propanol
$CH_3.CH_2.CHOH.CH_3$	*sec*-butyl alcohol	Ethylmethyl-carbinol	2-Butanol
$(CH_3)_3.COH$ *or* $^{3}CH_3{}^{2}\underset{\displaystyle CH_3}{\underset{|}{C}}(OH){}^{1}CH_3$	*tert.* butyl alcohol	Trimethylcarbinol	2-Methyl-2-propanol

When an alkanol loses the hydrogen atom of the —OH group, the residual group RO— is termed *alkoxy group*. For example, $CH_3O—$ is methoxy group and $C_2H_5O—$ is ethoxy group.

4. General Methods of Preparation.—Monohydric alcohols can be prepared by the following general methods :

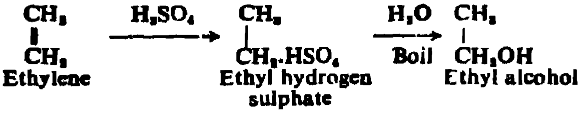
(1) *By the hydrolysis of an alkyl halide with aqueous alkali or silver oxide suspended in water.*

$$\underset{\text{Ethyl iodide}}{C_2H_5\boxed{I \quad + \quad K}}\underset{(\textit{Aqueous})}{OH} \longrightarrow \underset{\text{Ethanol}}{C_2H_5OH} + KI$$

$$\underset{\substack{\text{Methyl}\\ \text{bromide}}}{CH_3\boxed{Br \quad + \quad Ag}}\underset{\substack{\text{Moist}\\ \text{silver oxide}}}{OH} \longrightarrow \underset{\substack{\text{Methyl}\\ \text{alcohol}}}{CH_3OH} + AgBr$$

For mechanism see page 1·151.

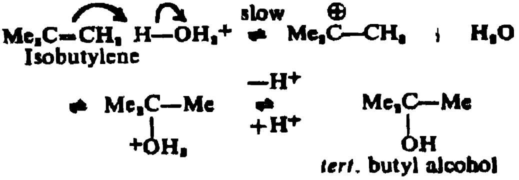
(2) *By Hydration of Olefins.* Olefins may be hydrated to alcohols by absorption in concentrated sulphuric acid followed by hydrolysis of alkyl hydrogen sulphate.



$$\underset{\text{Ethylene}}{\begin{matrix}CH_2\\ \| \\ CH_2\end{matrix}} \xrightarrow{H_2SO_4} \underset{\text{Ethyl hydrogen sulphate}}{\begin{matrix}CH_3\\ | \\ CH_2.HSO_4\end{matrix}} \xrightarrow[\text{Boil}]{H_2O} \underset{\text{Ethyl alcohol}}{\begin{matrix}CH_3\\ | \\ CH_2OH\end{matrix}}$$

This is one of the recent synthetic methods used for the industrial preparation of lower alcohols from olefins obtained from cracked petroleum. Alcohol obtained is mixed with some ether which is a by-product.

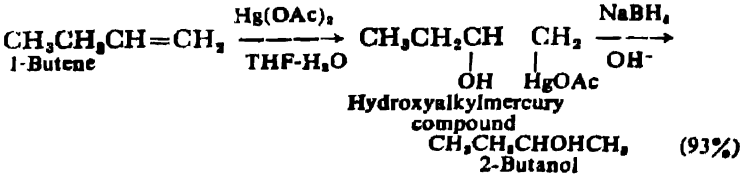
Olefins, however, may also be catalytically hydrated in dilute acid solution. Mechanism proposed for hydration is as follows :



$$\underset{\text{Isobutylene}}{Me_2C{=}CH_2}\ \ H{-}OH_2^+ \overset{\text{slow}}{\rightleftharpoons} Me_2\overset{\oplus}{C}{-}CH_3 + H_2O$$
$$\rightleftharpoons \begin{matrix}Me_2C{-}Me\\ | \\ {}^+OH_2\end{matrix} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} \underset{\textit{tert}.\ \text{butyl alcohol}}{\begin{matrix}Me_2C{-}Me\\ | \\ OH\end{matrix}}$$

Two indirect methods for addition of water to olefins are :

(*a*) *Oxymercuration-Demercuration.* Alkene is treated with mercuric acetate in water-tetrahydrofuran solution when hydroxyalkylmercury compound is obtained. This is reduced with $NaBH_4$ when alcohol is produced. Addition of water occurs according to Markownikoff's rule.



$$\underset{\text{1-Butene}}{CH_3CH_2CH{=}CH_2} \xrightarrow[\text{THF-}H_2O]{Hg(OAc)_2} \underset{\text{Hydroxyalkylmercury compound}}{\begin{matrix}CH_3CH_2CH & CH_2\\ | & | \\ OH & HgOAc\end{matrix}} \xrightarrow[OH^-]{NaBH_4} \underset{\text{2-Butanol}}{CH_3CH_2CHOHCH_3} \quad (93\%)$$

(*b*) *Hydroboration-Oxidation.* It has already been discussed on page 2·28.

$$3\,R{-}CH{=}CH_2 + \tfrac{1}{2}\,(BH_3)_2 \rightarrow (R{-}CH_2CH_2)_3\,B$$
$$\xrightarrow[OH^-,\ H_2O]{H_2O_2} 3RCH_2CH_2OH + B(OH)_3$$

Here addition of water takes place in anti-Markownikoff way.

(3) *By hydrolysis of esters with alkali.*

$$\underset{\text{Ester}}{RCO}\,\boxed{OR' + H}\,\underset{\text{Dil. alkali}}{ONa} \longrightarrow \underset{\text{Sod. salt}}{RCOONa} + \underset{\text{Alcohol}}{R'OH}$$

The method is important for industrial preparation of certain alcohols which occur naturally as esters.

Tertiary alkyl halides do not give a good yield of alcohol on hydrolysis. There is a greater tendency to form olefins than alcohols.

A good yield of alcohol can, however, be obtained by first converting the alkyl halide into an ester which is next hydrolysed to get tertiary alcohol.

$$\underset{\text{Tertiary alkyl halide}}{R_3CX} + \underset{\text{Silver acetate}}{CH_3COOAg} \xrightarrow[\text{solution}]{\text{In alcoholic}} \underset{\text{Ester}}{CH_3COO.CR_3} + AgX$$

$$CH_3COO|CR_3 + \underset{}{Na|OH} \longrightarrow \underset{\text{Tertiary alcohol}}{R_3COH} + CH_3COONa$$

(4) ***By hydrolysis of ether by heating with dilute sulphuric acid under pressure, e.g.,*** ethanol from diethyl ether.

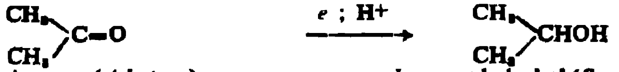
$$\underset{\text{Diethyl ether}}{C_2H_5OC_2H_5} + H_2O \xrightarrow[\text{under pressure}]{\text{Dil. }H_2SO_4} \underset{\text{Ethanol}}{2C_2H_5OH}$$

The method is used industrially for preparation of alcohols from ethers obtained as by-products during the preparation of certain alcohols.

(5) ***By reducing acid chlorides, aldehydes or ketones with*** *excess of* ***sodium*** and ethanol (*Bouveault-Blanc reduction*) ***or catalytically.***

$$\underset{\text{Acetyl chloride}}{CH_3COCl} \xrightarrow{e\ ;\ H^+} \underset{\text{Ethyl alcohol (Primary)}}{CH_3CH_2OH} + HCl$$

$$\underset{\text{Acetaldehyde}}{CH_3CH{=}O} \xrightarrow{e\ ;\ H^+} \underset{\text{Ethyl alcohol (Primary)}}{CH_3CH_2OH}$$



$$(CH_3)_2C{=}O \xrightarrow{e\ ;\ H^+} (CH_3)_2CHOH$$

Acetone (*A ketone*) Isopropyl alcohol (*Secondary*)

Lithium aluminium hydride, $LiAlH_4$ gives a very good yield of alcohols from aldehydes, ketones, esters, acids, acid chlorides and acid anhydrides in ethereal solutions. One advantage of this reagent is that it does not reduce the olefinic bond and hence can reduce unsaturated aldehydes, ketones, etc., to unsaturated alcohols.

$$\underset{\text{Aldehyde}}{RCH{=}O} \text{ or } \underset{\text{Ester}}{RCOOR} \text{ or } \underset{\text{Acid}}{RCOOH} \xrightarrow{LiAlH_4} \underset{\text{Primary alcohol}}{RCH_2OH}$$

$$\underset{\text{Ketone}}{R.CO.R} \xrightarrow{LiAlH_4} \underset{sec.\text{ alcohol}}{R.CHOH.R}$$

Lithium borohydride is another reducing agent but less vigorous. It may be used to reduce more reactive groups when two or more such groups are present in the molecule, *e.g.*, out of carbonyl and carboxyl groups, the former is reduced preferentially.

$$R.CO.CH_2.CH_2.COOH \xrightarrow{LiBH_4} RCHOH.CH_2.CH_2COOH$$

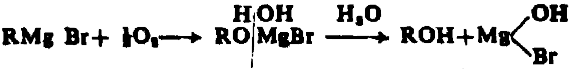
(6) ***By the action of nitrous acid on primary amines.***

$$\underset{\substack{\text{Ethylamine}\\ \text{(Primary amine)}}}{\begin{array}{l|l|l} HO & N & O \\ C_2H_5 & N & H_2 \end{array}} + \underset{\text{Nitrous acid}}{HONO} \longrightarrow \underset{\substack{\text{Ethanol}\\ \text{(An alcohol)}}}{C_2H_5OH} + N_2 + H_2O$$

(7) ***With the help of Grignard reagent.*** Primary, secondary and tertiary alcohols may be prepared by means of a Grignard

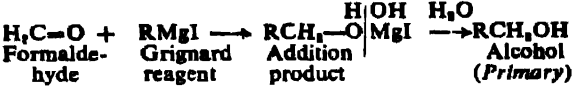
reagent and an appropriate carbonyl compound (an aldehyde or a ketone). The addition product first formed is decomposed with water to give alcohol.

(*i*) ***Primary alcohols*** **are obtained** with dry **oxygen or formaldehyde.**



$$RMgBr + \tfrac{1}{2}O_2 \longrightarrow \overset{H|OH}{RO|MgBr} \xrightarrow{H_2O} ROH + Mg\begin{smallmatrix}OH\\Br\end{smallmatrix}$$

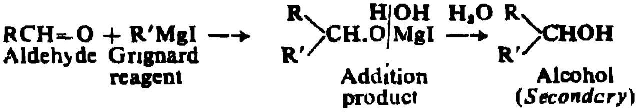
(*v.g.*)



$$\underset{\text{Formaldehyde}}{H_2C{=}O} + \underset{\text{Grignard reagent}}{RMgI} \longrightarrow \underset{\text{Addition product}}{\overset{H|OH}{RCH_2{-}O|MgI}} \xrightarrow{H_2O} \underset{\text{Alcohol (Primary)}}{RCH_2OH}$$

(*g.*)

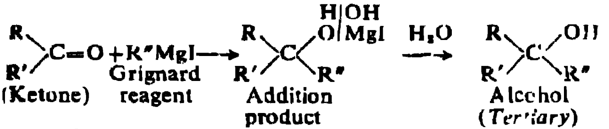
(*ii*) *Secondry alcohols* are prepared with aldehydes other than formaldehyde.



$$\underset{\text{Aldehyde}}{RCH{=}O} + \underset{\text{Grignard reagent}}{R'MgI} \longrightarrow \underset{\text{Addition product}}{\overset{H|OH}{\begin{smallmatrix}R\\R'\end{smallmatrix}{>}CH.O|MgI}} \xrightarrow{H_2O} \underset{\text{Alcohol (Secondary)}}{\begin{smallmatrix}R\\R'\end{smallmatrix}{>}CHOH}$$

(*f.g.-g.*)

(*iii*) *Tertiary alcohols* may be prepared with ketones.



$$\underset{\text{(Ketone)}}{\begin{smallmatrix}R\\R'\end{smallmatrix}{>}C{=}O} + \underset{\text{Grignard reagent}}{R''MgI} \longrightarrow \underset{\text{Addition product}}{\begin{smallmatrix}R\\R'\end{smallmatrix}{>}C{<}\begin{smallmatrix}\overset{H|OH}{O|MgI}\\R''\end{smallmatrix}} \xrightarrow{H_2O} \underset{\text{Alcohol (Tertiary)}}{\begin{smallmatrix}R\\R'\end{smallmatrix}{>}C{<}\begin{smallmatrix}OH\\R''\end{smallmatrix}}$$

(*g.*)

(8) *By fermentation.* A number of alcohols are obtained by fermentation process (*see* manufacture of ethanol by fermentation of molasses).

(9) *Synthetic methods.* Various synthetic methods which have become very important in recent years for the manufacture of alcohols are :

(*i*) *By hydration of olefins. See* method (2) given above.

(*ii*) ***From carbon monoxide and hydrogen.*** A mixture of carbon monoxide and hydrogen is heated under pressure in the presence of catalyst (zinc chromite + small amount of iron salts). A mixture of lower alcohols (*e.g.*, CH_3OH, C_2H_5OH, *n*-propyl and isobutyl alcohols, etc.) is obtained. Individual members are separated by fractional distillation of the mixture.

(*iii*) *By the "oxo" process from olefins.* Carbon monoxide, hydrogen and the olefin are passed under pressure (200 atm) over a heated catalyst (398-418K). The catalyst consists of a mixture of cobalt, thoria, magnesia and kieselguhr in the ratio 40 : 2 : 3 : 80. For example, propylene gives *n*- and *sec*-butyl alcohols.

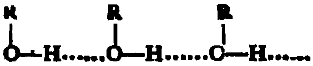
(*iv*) ***By oxidation of natural gas.*** Lower alcohols are industrially prepared by the oxidation of natural gas.

5. General Properties of Alcohols.—

(*a*) **Physical.** (*i*) The alcohols are *neutral* substances.

(*ii*) The lower members of the homologous series are colourless mobile liquids and are followed by those of oily consistency up to $C_{11}H_{23}OH$. Higher members are colourless waxy solids.

In a group of isomeric alcohols, primary alcohol has the higher boiling point and the tertiary the lowest. The boiling points of liquid alcohols are higher than those expected from their molecular weights. This is believed to be due to association of their molecules through hydrogen bonding giving rise to big molecules with low volatility as given below :



$$\overset{R}{\underset{|}{}}O—H......\overset{R}{}O—H......\overset{R}{}O—H......$$

On comparing the boiling points of alcohols with those of hydrocarbons of roughly the same molecular mass, we find that alcohols boiled at much higher temperatures.

Compound	Mol. mass	B.P.(K)	Compound	Mol. mass	B.P.(K)
CH_3OH	32	338	C_2H_5OH	46	351·5
CH_3CH_3	30	184·4	C_3H_8	44	228·5

Boiling point of methanol is about 154° higher than that of ethane even though their molecular masses are almost the same. Similarly, boiling point of ethanol is 123° higher than that of propane.

This is due to the presence of strong hydrogen bonds resulting in association in alcohol which are absent in alkanes.

(*iii*) Lower members are soluble in water and organic solvents, but the solubility in water goes on decreasing with the rise of molecular weight.

Their solubility in water is due to the fact that the oxygen atom of the hydroxyl group in alcohols can form hydrogen bonds with water molecules. In the lower alcohols the —OH group constitutes a large part of the molecule and they are more soluble. In higher alcohols the hydrocarbon character of the molecule increases and hence the solubility in water decreases. But the structure of the carbon chain also plays a part, *e.g.*, *n*-butyl alcohol is fairly soluble in water whereas *tert.* butyl alcohol is miscible with water in all proportions.

(*iv*) Lower members have a pleasant smell but a burning taste and the higher ones are odourless and tasteless.

(*v*) These are lighter than water.

(*vi*) Their boiling points rise fairly uniformly with a rise in molecular weight. For isomeric alcohols the boiling points are in the order : primary alcohol > secondary > tertiary.

(*vii*) Lower alcohols give solid derivatives with certain metallic salts. In these alcohol molecules are a part of the constitution like water of crystallization. For example :

$CaCl_2.4CH_3OH$ $CaCl_2.4C_2H_5OH$

$MgCl_2.6CH_3OH$ $MgCl_2.6C_2H_5OH$

(*b*) **Chemical.** The monohydric alcohols are commonly regarded as derivates of alkanes obtained by the replacement of one hydrogen atom by hydroxyl group. They can also be regarded with equal propriety, as derived from water by replacement of the hydrogen atom by alkyl group, *e.g.*,

$$\begin{array}{ccccc} CH_4 & \xrightarrow[\text{of H by —OH}]{\text{Replacement}} & CH_3—OH & \xleftarrow[\text{of H by } CH_3]{\text{Replacement}} & H—OH \\ \text{Methane} & & \text{Methanol} & & \text{Water} \end{array}$$

Alcohols, therefore, inherit properties of both parents—alkanes and water. For example, physical properties of methanol lie between those of methane and water as given below :

Property	*Methane*	*Methanol*	*Water*
m.p.	89K	176·8K	273K
b.p.	159K	338K	373K
Density	0·415 (109K)	0·792	1·00
Solubility	Insoluble in water ; soluble in hydrocarbons	Freely soluble in water ; fairly in hydrocarbons	Immiscible with hydrocarbons

In chemical reactions also, alcohols bear a striking resemblance to water and alkanes as given below :

1. REACTIONS INVOLVING REPLACEMENT OF HYDROGEN ATOM OF THE HYDROXYL GROUP :

(*i*) **Action of alkali metals—sodium, potassium or lithium.** The hydrogen atom of the hydroxyl group (—OH) is replaced by an atom of metal with the evolution of hydrogen and *alkoxide is formed.*

$$\underset{\text{Alcohol}}{2ROH} + 2Na \longrightarrow \underset{\text{Sod alkoxide}}{2RONa} + H_2$$

$$\underset{\text{Ethanol}}{2C_2H_5OH} + 2Na \longrightarrow \underset{\text{Sod ethoxide}}{2C_2H_5ONa} + H_2$$

Alkoxides (RO^-Na^+) are electrovalent compounds which are readily decomposed by water.

$$RONa + H_2O \rightarrow ROH + NaOH$$

The order of the ease of formation of alkoxides is :

Primary alcohol ⊳ secondary ⊳ tertiary.

This may be explained as follows : There are two possible ways in which the group COH may undergo fission :

$$C \vdots —O—H \quad \text{and} \quad C—O \vdots H$$

In C—O—H the shared electron pairs are displaced towards oxygen due to its higher electronegativity as compared to carbon and hydrogen, *i.e.*, we have

$$\overset{\delta+}{C} \rightarrow \overset{\delta-}{O} \leftarrow \overset{\delta+}{H}$$

The greater the displacement of the shared pair towards oxygen atom in the C—O, the larger is the negative charge on the oxygen atom and weaker is its attraction of the shared pair of the O—H bond.

In other words, the greater the polarity of C—O bond the smaller the olarity of O—H bond. But the strength of a bond decreases as its polarity

Since alkyl groups are electron-releasing, the larger the number of alkyl groups attached to the carbon atom of C—O—H group, the greater will be the polarity of the C—O bond, *i.e.*, the polarity of the C—O bond is the greatest in tertiary alcohols and the least in primary alcohols.

Consequently the polarity of the O—H bond is the smallest in tertiary alcohols and greatest in primary alcohols. In other words, strength of C—O bond is least in tertiary alcohols and greatest in primary alcohols while the strength of O—H bond is greatest in tertiary alcohols and smallest in primary alcohols.

Consequently tendency to break as C ⋮ —O—H is greatest in tertiary alcohols and least in primary alcohols.

Conversely tendency to break as C—O— ⋮ H (as in the formation of alkoxides) is greatest in primary alcohols and least in tertiary alcohols.

(*ii*) **Action of Organic acids.** Alcohols react with organic acids to form *esters*. The process is called *esterification** which unlike neutralization is a reversible, non-ionic and slow process generally carried out in the presence of a dehydrating agent. Concentrated sulphuric acid is commonly used since it acts as a protonating agent as well as a dehydrating agent.

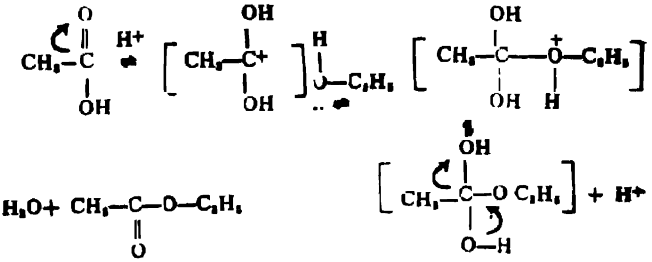
$$\underset{\text{Organic acid}}{RCO|\overline{OH + H}|} \underset{\text{Alcohol}}{OR'} \rightleftharpoons \underset{\text{Ester}}{RCOOR'} + H_2O$$

$$\underset{\text{Acetic acid}}{CH_3CO|\overline{OH + H}|} \underset{\text{Ethanol}}{OC_2H_5} \rightleftharpoons \underset{\text{Ethyl acetate (Ester)}}{CH_3COOC_2H_5} + H_2O$$

This involves breaking of COH group as C—O— ⋮ H. The order of reactivity of an alcohol with given organic acid is, therefore, as :

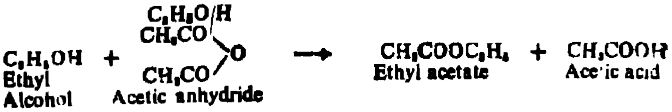
Primary alcohol > secondary > tertiary.

Mechanism of the reaction is as follows :



(*iii*) **Acetylation.** When an alcohol is treated with acetyl chloride (CH_3COCl) or acetic anhydride, the H-atom of the —OH group is replaced by an acetyl group. The process is called *acetylation*.

$$\underset{\text{Acetyl chloride}}{CH_3CO|\underline{Cl \quad + \quad H}|} \underset{\text{Ethanol}}{OC_2H_5} \longrightarrow \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + HCl$$



In fact, an alcohol will react with any acid chloride, RCOCl or anhydride and the process is known as *acylation*.

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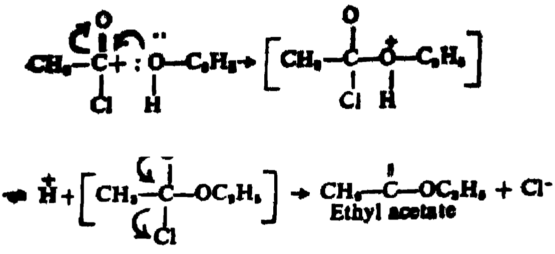
* The old method of formulating esterification as

$$RCOO|\overline{H + HO}|R' \rightleftharpoons RCOOR' + H_2O$$

was proved to be incorrect by Roberts, Urey (1938) and others.

The mechanism of the reaction is as follows :



(Nucleophilic attack of alcohol on acid chloride)

(*iv*) **Action of Grignard reagents.** Hydrocarbons are obtained **when** *alcohols react with* Grignard reagents.

$$\underset{\text{Alcohol}}{\text{RO}|\overline{\underline{\text{H}}}} \;\overline{\underline{+\;}}\; \underset{\text{Ethylmagnesium iodide}}{\overline{\underline{\text{C}_2\text{H}_5}}|\text{MgI}} \longrightarrow \underset{\text{Ethane}}{\text{C}_2\text{H}_6} + \text{RO.MgI}$$

2. **R**EACTIONS INVOLVING REPLACEMENT OF THE HYDROXYL GROUP :

(*i*) **Action of halogen acids.** Alcohols react with halogen **acids** to give halides, *e g.*, an iodide is obtained with hydriodic acid **and a** chloride with hydrochloric acid.

$$\underset{\text{Ethyl alcohol}}{\text{C}_2\text{H}_5|\overline{\underline{\text{OH}}}} \;\overline{\underline{+\;\;\text{H}}}|\underset{\text{Hydrochloric acid (mineral acid)}}{\text{Cl}} \xrightleftharpoons{\text{ZnCl}_2} \underset{\text{Ethyl chloride}}{\text{C}_2\text{H}_5\text{Cl}} + \text{H}_2\text{O}$$

If, however, an alcohol is heated with concentrated hydriodic **acid and** red phosphorus, it is converted into a paraffin.

$$\underset{\textit{Ethanol}}{\text{C}_2\text{H}_5\text{OH}+2HI} \xrightarrow{\text{Red P}} \underset{\text{Ethane}}{\text{C}_2\text{H}_6} + \text{I}_2+\text{H}_2\text{O}$$

The order of reactivity of the halogen acids is *HI>HBr>HCl.*

The order of reactivity of an alcohol with a given halogen **acid is :**

tertiary alcohol > secondary > primary.

We see that this order is a reverse of the order of reactivity **with** an organic acid. This implies that *the mechanism of esterification of organic acid is different from that of halogen acids.* We have **already** represented them differently as follows :

$$\text{CH}_3\text{CO}|\overline{\underline{\text{OH} \;\;+\;\; \text{H}}}|\,\text{OC}_2\text{H}_5 \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}$$
$$\text{C}_2\text{H}_5|\overline{\underline{\text{OH} \;\;+\;\; \text{H}}}|\,\text{Cl} \rightleftharpoons \text{C}_2\text{H}_5\text{Cl} + \text{H}_2\text{O}$$

Mechanism of Reaction. Most primary alcohols react by an S_N2 mechanism, while secondary and tertiary alcohols react by an S_N1 mechanism. The commonly accepted mechanism supposes the reaction to take place in the following three steps :

(A) For secondary and tertiary alcohols :

(*a*) *Protonation of alcohol.* This converts the poor leaving group, —OH to the good leaving group, $^{-}\text{OH}_2{}^{+}$.

$$\text{ROH} + \text{HX} \rightleftharpoons \text{R}\overset{+}{\text{O}}\text{H}_2 + \text{X}$$

(*b*) ***Formation of carbocation***

$$\underset{\text{Protonated alcohol}}{R\overset{+}{O}H_2} \rightleftharpoons \underset{\text{Carbocation}}{\overset{+}{R}} + H_2O$$

This is the most difficult step as it involves the breaking of C—OH bond (alkyl-oxygen fission). The *tertiary carbocation* being most stable is formed most readily while the primary carbocation being the least stable is formed least readily. The rearrangement of the carbocation may take place (by migration of H or R from one C to another) to form a more stable carbocation.

(*c*) The carbocation (the originally formed one or the one formed after rearrangement) unites with a halide ion to form alkyl halide.

$$\overset{+}{R} + \overset{-}{X} \longrightarrow RX$$

Examples of rearrangement of carbocations are given on page 1·149.

(B) For primary alcohols :

(*a*) *Protonation of alcohols as given* under (A)

(*b*) *Nucleophilic substitution.*

$$X^{\ominus} + R-\overset{\oplus}{O}H_2 \dashrightarrow X-R + H_2O$$

The tendency for an S_N1 mechanism is enhanced in a medium like anhydrous $ZnCl_2$ in conc HCl (*Lucas reagent*) and the order of reactivity has been found to be :

$$> \quad 2° \quad > \quad 1°$$

immediate reaction	reaction within 5 minutes	no reaction at room temp.

(*ii*) **Action of phosphorus halides—PCl_5, PCl_3, PBr_3 (P_4+Br_2), PI_3, (P_4+I_2).** The hydroxyl group is replaced by the corresponding halogen atom and an alkyl halide is formed.

$$\underset{\text{Alcohol}}{ROH} + PCl_5 \longrightarrow \underset{\text{Alkyl halide}}{RCl} + POCl_3 + HCl$$

$$\underset{\text{Ethyl alcohol}}{3C_2H_5OH} + PCl_3 \longrightarrow \underset{\text{Ethyl chloride}}{3C_2H_5Cl} + H_3PO_3$$

$$\underset{\text{Methyl alcohol}}{3CH_3OH} + PI_3 \xrightarrow{P_4+I_2} \underset{\text{Methyl iodide}}{3CH_3I} + H_3PO_3$$

3. REACTIONS INVOLVING BOTH ALKYL GROUP AND HYDROXYL GROUP :

(*i*) **Dehydration.** Alcohols may be dehydrated to the corresponding olefins—the carbon atom adjacent to the COH group loses one hydrogen atom. The order of ease of dehydration is :

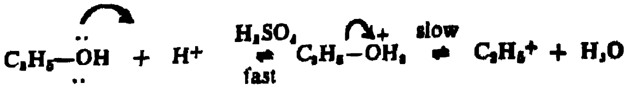
tertiary alcohol > secondary > primary.

Alcohols are dehydrated by simple heating (670-1070K) or passing the vapours over alumina at 620K.

$$\underset{\text{Ethanol}}{CH_3-CH_2OH} \xrightarrow[-H_2O]{Al_2O_3,\ 620K} \underset{\text{Ethylene}}{CH_2=CH_2}$$

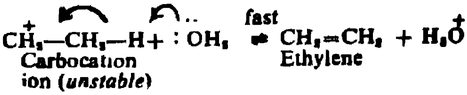
Primary alcohols are dehydrated by concentrated sulphuric acid at about 440K. Dilute sulphuric acid is used with secondary and tertiary alcohols to avoid polymerization of the ole

It appears that the function of the catalyst is to weaken the C—O bond of the C—OH group. With sulphuric acid the mechanism may be



$$C_2H_5-\ddot{O}H + H^+ \underset{fast}{\overset{H_2SO_4}{\rightleftharpoons}} C_2H_5-\overset{+}{O}H_2 \overset{slow}{\rightleftharpoons} C_2H_5^+ + H_2O$$

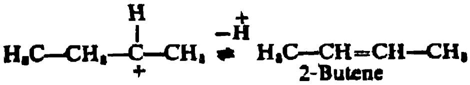
A proton from the acid coordinates with the oxygen atom. The polarity of the C—O bond increases and its strength decreases. Rupture of C—O bond produces the carbocation and a molecule of water. The carbocation, which is unstable, stabilises itself by eliminating a proton to form ethylene (olefin) and the proton is accepted by a water molecule.



$$\overset{+}{C}H_2-CH_2-H + :\ddot{O}H_2 \overset{fast}{\rightleftharpoons} CH_2=CH_2 + H_3\overset{+}{O}$$

Carbocation ion (*unstable*) Ethylene

Expulsion of H^+ takes place in such a manner as to form a more stable alkene and if necessary may be *preceded* by rearrangement of carbocation as stated in the mechanism of ROH and HX. *Alkene that is most highly substituted is preferred.* For example, *sec.* butyl carbocation gives 2-butene.



$$H_3C-CH_2-\overset{H}{\underset{+}{C}}-CH_3 \overset{-\overset{+}{H}}{\rightleftharpoons} H_3C-CH=CH-CH_3$$

sec. Butyl carbocation 2-Butene

2-Butene is preferred and not $H_3C.CH_2.CH=CH_2$ as this is less highly substituted at the C atoms separated by the double bond.

Action between ethanol and sulphuric acid is interesting, as different products are obtained under different conditions. Ethyl hydrogen sulphate is the first product of reaction when ethanol is treated with concentrated sulphuric acid in cold.

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + H_2SO_4 \longrightarrow \underset{\text{Ethyl hydrogen sulphate}}{C_2H_5HSO_4} + H_2O$$

(*a*) Ethyl sulphate is obtained by distilling the ethyl hydrogen sulphate under reduced pressure.

$$2C_2H_5HSO_4 \longrightarrow (C_2H_5)_2SO_4 + H_2SO_4$$

(*b*) In the presence of excess of alcohol ethyl hydrogen sulphate further reacts at 410K to give ether.

$$\underset{\text{Ethyl hydrogen sulphate}}{C_2H_5\boxed{HSO_4 + H}} \underset{\text{Excess of alcohol}}{OC_2H_5} \xrightarrow{410K} \underset{\text{Diethyl ether}}{C_2H_5-O-C_2H_5} + H_2SO_4$$

(*c*) In the presence of excess of sulphuric acid ethyl hydrogen sulphate loses a molecule of sulphuric acid at 440K to give ethylene.

$$\underset{\text{Ethyl hydrogen sulphate}}{C_2H_5HSO_4} \xrightarrow[\text{Excess of } H_2SO_4]{440} \underset{\text{Ethylene}}{CH_2=CH_2} + H_2SO_4$$

Methanol gives reactions with sulphuric acid similar to ethanol except the reaction corresponding to (*c*) above.

Dehydration of secondary and tertiary alcohols may occur in two different ways, *e.g.*,

$$CH_3.CH_2.CHOH.CH_3 \xrightarrow{-H_2O} \left| \begin{array}{l} \rightarrow CH_3.CH_2.CH{=}CH_2 \\ \quad\quad \text{1-Butene} \\ \rightarrow CH_3CH{=}CH.CH_3 \\ \quad\quad \text{2-Butene} \end{array} \right.$$

In general it has been found that hydrogen attached to the adjacent carbon atom joined to least number of hydrogen atoms is eliminated most easily, *i.e.*, elimination of water molecule is in accordance with Saytzeff rule. Thus in the above reaction 2-butene is the main product.

In case the carbon atom adjacent to COH carries no hydrogen atoms, dehydration is accompanied by molecular rearrangement. *e.g.*, dehydration of 2,2-dimethyl-1-propanol gives 2-methyl-2-butene

$$(CH_3)_3C.CH_2OH \xrightarrow{-H_2O} (CH_3)_2C{=}CH.CH_3$$

For mechanism see page 1·153.

(*ii*) **Oxidation**. Alcohols can be oxidised and the products of oxidation depend on the class of alcohol (*Refer to section 7*).

(*iii*) **Action of hot reduced copper**. Here again the products depend on the class of alcohol (*see* page 2·134).

(*iv*) **Action of chlorine**. Chlorine acts both as an oxidising agent and a chlorinating agent. For example, with ethanol it gives chloral.

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[\text{Oxidation}]{Cl_2} \underset{\text{Acetaldehyde}}{CH_3.CHO} \xrightarrow[\text{Chlorination}]{Cl_2} \underset{\text{Chloral}}{CCl_3CHO}$$

6. **Tests for Hydroxyl Group.**—The following tests may be applied to detect the presence of a hydroxyl group in an unknown organic compound. In case the compound is a solid, its solution is to be prepared in an inert organic solvent, *e.g.*, benzene or dry ether.

(*i*) **Sodium metal test**. Add sodium metal to the substance or its solution. Bubbles of hydrogen gas, if evolved, indicate the presence of an OH group in the given substance.

(*ii*) **Phosphorus pentachloride test**. Add phosphorus pentachloride to the given substance or its solution. If it becomes warm with the evolution of hydrogen chloride, the given substance contains a hydroxyl group.

(*iii*) **Acylation test**. To the given substance or its solution add acetyl chloride or benzoyl chloride. If hydrogen chloride gas is liberated, it shows that the given substance is a hydroxy compound. Separation of an oily layer of ester, if there, is an additional point in favour of the inference.

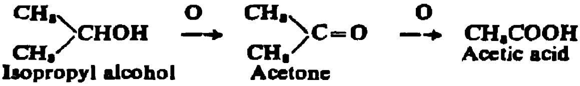
7. **Distinction between Primary, Secondary and Tertiary Alcohols.**—The following methods are employed for distinguishing the three classes of alcohols from one another :

(1) **Oxidation Method.** The nature of the oxidation product depends on whether the alcohol is primary, secondary or tertiary.

(*i*) A primary alcohol is easily oxidised to an aldehyde and then to an acid both containing the same number of carbon atoms as the original alcohol. For example, ethyl alcohol is oxidised to acetaldehyde which is further oxidised to acetic acid.

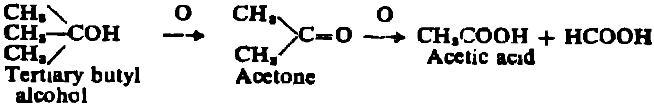
$$\underset{\text{Ethyl alcohol}}{CH_3{-}CH_2OH} \xrightarrow{O} \underset{\text{Acetaldehyde}}{CH_3{-}CHO} \xrightarrow{O} \underset{\text{Acetic acid}}{CH_3COOH}$$

(*ii*) A secondary alcohol on oxidation gives first a ketone with the same number of carbon atoms as the original alcohol. Ketones are fairly difficult to oxidise but on prolonged action of oxidising agents, they undergo fission to yield a mixture of acids each containing fewer carbon atoms than the original alcohol. For example, isopropyl alcohol gives first acetone and then acetic acid.



$$\underset{\text{Isopropyl alcohol}}{(CH_3)_2CHOH} \xrightarrow{O} \underset{\text{Acetone}}{(CH_3)_2C{=}O} \xrightarrow{O} \underset{\text{Acetic acid}}{CH_3COOH}$$

(*iii*) A tertiary alcohol is resistant to oxidation in neutral or alkaline solution but is readily oxidised by an acid oxidising agent to give a mixture of ketone and acid each with fewer number of carbon atoms than the original alcohol.



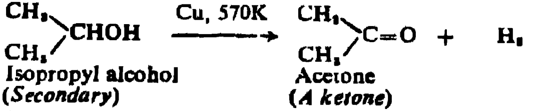
$$\underset{\text{Tertiary butyl alcohol}}{(CH_3)_3C{-}OH} \xrightarrow{O} \underset{\text{Acetone}}{(CH_3)_2C{=}O} \xrightarrow{O} \underset{\text{Acetic acid}}{CH_3COOH} + HCOOH$$

The oxidising agents usually employed for oxidation of alcohols are : acid dichromate, acid or alkaline potassium permaganate and dilute nitric acid.

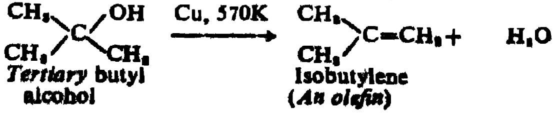
Thus oxidising the given alcohol and analysing the products of oxidation will indicate whether it is primary, secondary or a tertiary alcohol.

(2) **By the action of hot reduced copper.** Primary, secondary and tertiary alcohols differ in their behaviour towards hot reduced copper at 570K. A primary alcohol loses hydrogen and gives an aldehyde ; a secondary alcohol loses hydrogen and gives a ketone ; while a tertiary alcohol loses water and gives an olefin. For example :

$$\underset{\substack{\text{Ethyl alcohol}\\(\textit{Primary})}}{CH_3CH_2OH} \xrightarrow{\text{Cu, 570K}} \underset{\substack{\text{Acetaldehyde}\\(\textit{An aldehyde})}}{CH_3CHO} + H_2$$



$$\underset{\substack{\text{Isopropyl alcohol}\\(\textit{Secondary})}}{(CH_3)_2CHOH} \xrightarrow{\text{Cu, 570K}} \underset{\substack{\text{Acetone}\\(\textit{A ketone})}}{(CH_3)_2C{=}O} + H_2$$



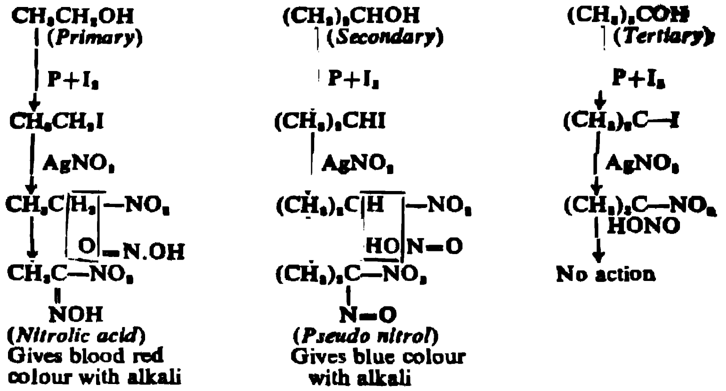
$$\underset{\substack{\text{Tertiary butyl}\\\text{alcohol}}}{(CH_3)_3C{-}OH} \xrightarrow{\text{Cu, 570K}} \underset{\substack{\text{Isobutylene}\\(\textit{An olefin})}}{(CH_3)_2C{=}CH_2} + H_2O$$

Thus the product obtained will indicate the nature of the original alcohol.

(3) **Victor Meyer's Method.** The given *alcohol* is converted into *an iodide* with phosphorus and iodine, which is then changed to a *nitroparaffin* with silver nitrite.

The nitro compound is now treated with an alkaline solution of sodium nitrite, acidified with hydrochloric acid, finally made alkaline with hydroxide solution. Nitrous acid from sodium nitrite and hydrochloric acid differently with the nitro compounds obtained from three classes of alcohols.

A blood red colour indicates a primary alcohol, a blue colour a secondary alcohol while no colour indicates a tertiary alcohol. The chemistry of reaction can be explained as given below :



(4) **By relative reactivities of the alcohols with hydrochloric acid** (*the Lucas test*). Lower alcohols are soluble in the *Lucas reagent* (a mixture of conc. HCl and anhydrous $ZnCl_2$). On adding the alcohol to Lucas reagent, a tertiary alcohol reacts immediately, a secondary alcohol reacts within about five minutes. The insoluble chloride is precipitated in each case. A primary alcohol does not react with the reagent at room temperature.

Thus on adding the given alcohol to the Lucas reagent if a precipitate appears immediately, it is a tertiary alcohol. If a precipitate appears after a few minutes it indicates that the alcohol is secondary. In case no precipitate is obtained in cold, the alcohol is primary.

8. Spectroscopic Identification of Alcohols.—

(*a*) **IR Spectrum.** Alcohols give characteristic absorption (O—H stretch) in the region 3650-3580 cm^{-1} (*v*) if the alcohol is not associated as a result of hydrogen bonding. Inter-molecular hydrogen bonding produces broad absorption band in the region 3550-3230 cm^{-1} (*v*) whereas in the case of intramolecular hydrogen bonding absorption appears in the region 3590-3420 cm^{-1} (*v*).

(C—O stretching vibrations seen are : primary alcohol $\sim$ 1050 cm^{-1} (*s*), secondary alcohol $\sim$ 1100 cm^{-1} (*s*) and tertiary alcohol $\sim$ 1150 cm^{-1}(*s*).

(*b*) **NMR Spectrum.** In NMR spectrum too the chemical shift of the hydroxyl proton is influenced by the hydrogen bonding.

It varies with temperature, concentration, and the nature of the solvent used. Ordinarily, the hydroxyl proton signal may appear anywhere in the range τ 5-9 (δ 1-5). As a result of hydrogen bonding this is shifted downfield.

The NMR spectrum of the hydroxyl proton is a singlet since it is not split by the neighbouring protons. The hydroxyl proton itself does not split the signals of the neighbouring proton. This is because of the very fast proton exchange going on among the various molecules of the same alcohol.

The protons of the alkyl group show chemical shift in the range τ 6—6·6 (δ 3·4—4). It appears that oxygen atom on account of its electron-withdrawing inductive effect causes a downfield shift of the neighbouring protons.

INDIVIDUAL MEMBERS

9. Methyl alcohol, Carbinol or Methanol, CH_3OH.—The first member of the homologous series of alcohols is called methyl alcohol, methanol or carbinol. It is also known as wood-spirit or wood naphtha as the earliest method for its preparation was by the destructive distillation of wood. It occurs in the combined state in some essential oils, *e.g.*, in oil of wintergreen, it occurs as methyl salicylate.

10. Manufacture.—Methyl alcohol can be prepared by any of the general methods for preparation of alcohols. It was at one time manufactured by destructive distillation of wood. This method is, however, obsolete now. Today most methyl alcohol is manufactured by the following synthetic methods :

(*i*) **From Water Gas.** Water gas is a mixture of carbon monoxide and hydrogen obtained by blowing steam over red hot coke.

$$\underset{\text{Red hot coke}}{C} + \underset{\text{Steam}}{H_2O} \longrightarrow \underset{\text{Water gas}}{CO+H_2}$$

Water gas is mixed with half its volume of hydrogen, compressed to about 200 atmospheres pressure and passed over a catalyst consisting of the oxides of copper, zinc and chromium at 570K.

$$CO + 2H_2 \longrightarrow CH_3OH$$

Methanol obtained is more than 99 per cent pure and if proper precautions are taken, its yield is almost 100 per cent.

(*ii*) **By the Catalytic Oxidation of Methane.** A mixture of methane (9 volumes) and oxygen (1 volume) is compressed to about 100 atmospheres pressure and passed through a copper tube at 470K.

$$\underset{\text{Methane}}{2CH_4} + O_2 \longrightarrow \underset{\text{Methanol}}{2CH_3OH}$$

11. Properties of Methyl Alcohol.—Methanol is a colourless, inflammable liquid (b.p. 338K). It is poisonous in nature and when taken internally causes blindness and even death. It burns with a faintly luminous flame. With air or oxygen, its vapours form an explosive mixture. It is miscible with water in all proportions and is miscible with many organic solvents. With calcium chloride it forms a solid derivative $CaCl_2.4CH_3OH$ and cannot, therefore, be dried over calcium chloride (*cf.* ethanol). It gives typical reactions of a monohydric primary alcohol.

12. Uses.—(*i*) Methanol is used :

(*i*) As a solvent for paints, varnishes, shellac, gums, celluloid cement, etc.

(*ii*) For denaturing alcohol—rendering it unfit for drinking purposes. Methylated spirit is denaturated ethanol used for purposes other than drinking.

(*iii*) In the manufacture of dyes, drugs, perfumes and formaldehyde (used in plastic industry).

(*iv*) For making automobile antifreeze mixtures.

(*v*) As one of the constituents of an alcohol-petrol fuel.

13. Tests.—(*i*) When warmed with a few drops of concentrated sulphuric acid and a little salicylic acid, methanol gives a characteristic fragrant smell of methyl salicylate.

(*ii*) On lowering a red hot copper spiral in methanol contained in a test-tube, a pungent odour of formaldehyde is obtained and the copper spiral becomes bright due to reduction.

(*iii*) Methanol does not give the iodoform reaction—distinction from ethanol and acetone.

14. Ethyl Alcohol, Ethanol (Methylcarbinol), C_2H_5OH.—Ethyl alcohol is the most important member of the alcohol series and is simply known as alcohol, rather the homologous series—alcohols, gets its name from this member. It is known in commerce as *spirit of wine* or *grain alcohol.* It can be prepared by any of the general methods for the preparation of primary alcohols.

15. Manufacture of Alcohol.—Different methods employed for the industrial preparation of alcohol are :

(*i*) **From Ethylene.** Ethylene (from cracked petroleum) is compressed to 15-30 atmospheres pressure and absorbed in concentrated sulphuric acid (98 per cent) at 340-350K when ethyl hydrogen sulphate or ethyl sulphate is obtained.

$$C_2H_4 + H_2SO_4 \rightarrow C_2H_5HSO_4$$
$$C_2H_4 + C_2H_5HSO_4 \rightarrow (C_2H_5)_2SO_4$$

The reaction mixture is diluted with water and warmed when hydrolysis occurs and ethanol is obtained together with some ether as by-product.

$$C_2H_5/\boxed{HSO_4 + H}OH \rightarrow C_2H_5OH + H_2SO_4$$
$$(C_2H_5)_2SO_4 + 2H_2O \rightarrow 2C_2H_5OH + H_2SO_4$$

(*ii*) **Direct Hydration of Ethylene.** This is carried on in the presence of phosphoric acid (catalyst). Ethylene and water vapour at 770 K under 60 atm pressure are passed into a reactor containing solid phosphoric acid.

$$CH_2{=}CH_2 + H_2O \xrightarrow[770K,\ 60\ atm.]{H_3PO_4} CH_3CH_2OH$$

(*iii*) **From Acetaldehyde.** Ethanol is manufactured by catalytic reduction of acetaldehyde (from acetylene). Vapours of acetaldehyde are mixed with hydrogen and passed over finely divided nickel at 370-410K.

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + H_2 \xrightarrow{\text{Ni, 410K}} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

(*iii*) **By Fermentation.** The earliest method of preparing alcohol was by fermentation and this is still used for the manufacture of alcohol and alcoholic drinks (beer, wine, brandy, etc.). This has been discussed in detail under *Alcohol Industry.*

16. **Properties.**—Ethanol is a colourless, inflammable liquid with a spirituous odour and burning taste. It boils at 351·1K and freezes at 155K. It is miscible with water in all proportions. It is a very good solvent for fats and resins and is much in demand in industry for which purpose it is denatured by adding pyridine, etc., lest it should be used for human consumption, as it is then supplied free of excise duty.

When taken in, alcohol is readily oxidised by the system, and is, therefore, an important source of immediate energy. The blood begins to flow faster and dilates the blood vessels thus imparting a glow to the cheeks of a habitual drunkard.

It is a typical member of the alcohol series and its properties are the general properties of alcohols discussed already. Like methanol, it cannot be dried over anhydrous calcium chloride with which it gives $CaCl_2.4C_2H_5OH$.

17. **Uses.**—Besides it being an important beverage, ethyl alcohol finds a very extensive use in industry. It is used :

(*i*) In the **manufacture of** (*a*) paints and varnishes, (*b*) organic substances like ether, chloroform, iodoform, etc., (*c*) dyes, (*d*) transparent soaps, and (*e*) both alcohol and ether are used for the manufacture of smokeless powder.

(*ii*) As a *substitute for petrol* under the name *power alcohol.*

(*iii*) **As a fuel** in spirit lamps and stoves.

Solid alcohol sold in the market is a dispersion of alcohol in saturated calcium acetate with a little stearic acid.

(*iv*) For preserving biological specimens.

(*v*) For making automobile antifreeze mixture.

(*vi*) In scientific apparatus, *e.g.*, thermometers and spirit levels.

18. **Tests.**—(*i*) *Iodoform test.* When a few drops of alcohol are warmed with iodine and potassium hydroxide, yellow precipitate of iodoform with characteristic smell is obtained.

(*ii*) *Fruity odour test.* When alcohol is heated gently with sodium acetate and concentrated sulphuric acid, a characteristic fruity odour of ethyl acetate is obtained.

Ethanol can be distinguished from methanol by the fact that (*i*) ethanol gives iodoform reaction whereas methanol does not ; and (*ii*) ethanol gives acetic acid on oxidation while methanol gives formic acid. Formic acid, being a powerful reducing agent, is readily distinguished from acetic acid.

19. Ascent and Descent of Series and Typical Conversions in Alcohols.—

(*a*) **Conversion of methanol into ethanol** (*Ascent of series*). Different steps involved are :

$$\underset{\text{Methanol}}{CH_3OH} \xrightarrow{HI} \underset{\text{Methyl iodide}}{CH_3I} \xrightarrow{KCN} \underset{\text{Methyl cyanide}}{CH_3CN} \xrightarrow{4H}$$

$$\underset{\text{Ethylamine}}{CH_3CH_2NH_2} \xrightarrow{HONO} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

(*b*) **Conversion of ethanol into methanol** (*Descent of series*). Different steps involved are :

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{O} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{O} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{NaOH}$$

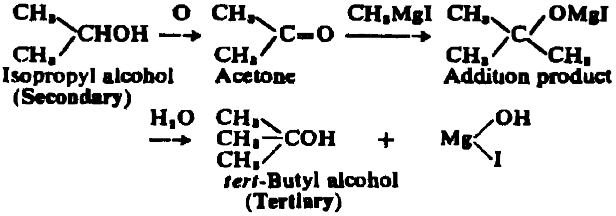
$$\underset{\text{Sod. acetate}}{CH_3COONa} \xrightarrow{\text{Soda-lime}} \underset{\text{Methane}}{CH_4} \xrightarrow{Cl_2} \underset{\text{Methyl chloride}}{CH_3Cl} \xrightarrow{AgOH} \underset{\text{Methanol}}{CH_3OH}$$

(*c*) **Conversion of Primary into Secondary alcohol**, *e.g.*, conversion of 1-propanol (*Primary*) into 2-propanol (*Secondary*)

$$\underset{\substack{\text{1-Propanol}\\ \text{(Primary alcohol)}}}{CH_3CH_2CH_2OH} \xrightarrow[\text{Conc. } H_2SO_4]{-H_2O} \underset{\text{Propylene}}{CH_3CH{=}CH_2}$$

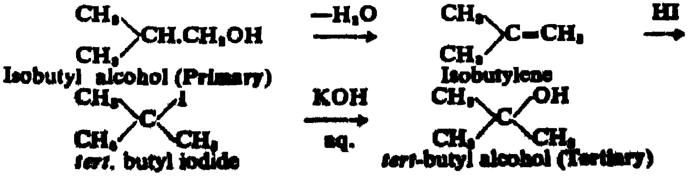
$$\xrightarrow{HI} \underset{\substack{\text{Isopropyl}\\ \text{iodide}}}{CH_3CHICH_3} \xrightarrow[\text{aq.}]{KOH} \underset{\substack{\text{2-Propanol}\\ \text{(Secondary alcohol)}}}{CH_3CHOHCH_3}$$

(*d*) **Conversion of Secondary into Tertiary alcohol.** Secondary alcohol is oxidised to ketone which is treated with a Grignard reagent to get tertiary alcohol. For example,



(*e*) **Conversion of Primary alcohol into Tertiary alcohol.** For this primary alcohol is first converted into secondary alcohol which is then converted into the tertiary alcohol, as given in (*c*) and (*d*) above.

A primary alcohol with a branched chain can be directly converted into tertiary alcohol as follows :



FERMENTATION

20. What is Fermentation ?—Slow decomposition of organic compounds like souring of milk, putrefaction of meat, preparation of wine and vinegar from cane juice are termed *Fermentation processes*. The process of fermentation was known to the prehistoric man. The *Somras* (सोमरस) of the ancient Hindus and the *Tari* (ताडी) of the Dravidians were certainly fermented liquors. The scientific nature of the process was, however, first explored by *Pasteur*[*] who considered it to be a purely physiological action carried out by the living organisms which in turn breathed out carbon dioxide. The living organisms bringing about fermentation are called *Ferments* which are obtained from vegetable or animal kingdom.

Liebig ridiculed Pasteur and wrote several articles under a pseudo name professing that the process was merely a chemical change and nothing more. Today we feel that the truth lies somewhere between the two extremes.

It is now believed that fermentation is brought about by non-living, complex, nitrogenous substances (called *Enzymes*) present in the body of living ferments. Fermentation reactions are generally accompanied by evolution of gases like carbon dioxide, methane and are exothermic.

21. Conditions favourable for Fermentation.—Various factors which influence the process of fermentation are :

(*i*) **Temperature.** At very high temperatures the ferments are destroyed while at very low temperature the reaction is extremely slow. There is a certain optimum temperature for every fermentation reaction, at which it proceeds most favourably. Generally 298-303K is the most favourable temperature.

(*ii*) **Presence of other substances.** Certain nutritive solutions—generally inorganic salt solutions—are added to act as food for the ferment cells.

(*iii*) **Absence of preservatives.** Substances like boric acid and mercury salts which retard the fermentation reaction are called preservatives. They destroy the ferments and should, therefore, be absent.

(*iv*) **Concentration.** Ferments are rendered inactive by high concentration of the solution to which these are added. The solutions used for fermentation should be sufficiently dilute to favour the fermentation reaction.

(*v*) **Aeration.** Mostly the fermentations proceed well only in the presence of air.

22. The Enzymes.—As stated earlier, enzymes are non-living, complex, nitrogenous substances present in living ferments. The action of the enzyme is more or less like that of a catalytic agent. It is definitely a selective and specific action. One enzyme can bring about only one chemical change, so much so, the enzyme—penicillium, glaucum, that attacks *d*-tartaric acid would not attack *l*-tartaric acid. Their activity is enhanced by the presence of another substance "*Co-enzyme*".

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[*] **Louis Pasteur (1822-95)**—French biologist, famous for his discovery of the part played by bacteria in fermentation.

The best results are achieved when the temperature is kept at about 300K. At too high or too low a temperature the reactivity of an enzyme stops short. A true catalyst is not used up in the reaction but enzymes gradually disappear in the process they bring about.

23. **A Few Common Enzymes.**—The following table gives the names, origin and functions of common enzymes :

Name	Origin	Function	Optimum Temperature
Diastase	Malt	Changes starch into malt sugar and dextrin.	330-340K
Maltase	Yeast	Changes malt sugar into glucose.	300K
Zymase	Yeast	Ferments glucose to alcohol and carbon dioxide.	300K
Invertase	Yeast	Inverts cane-sugar into glucose and fructose.	300K
Ptylin	Saliva	Changes starch into sugar.	310K
Acetobacter aceti	Mycoderma-aceti	Ferments alcohol into acetic acid.	300-315K
Pepsin	Gastric juice	Changes proteins into peptones.	310K

Tanning of leather, changing milk into curd, digestion and assimilation of food by the living system are only a few of the numerous activities that enzymes are responsible for in our daily life.

ALCOHOL INDUSTRY

24. **Manufacture of Ethanol by Fermentation.**—This is the earliest method used for industrial preparation of ethanol. The starting materials are : (*i*) cheap starchy materials like potatoes, maize, barley, rice, and (*ii*) molasses, a by-product in sugar industry.

Two different methods for the manufacture of ethanol are :

(A) FROM MOLASSES

Molasses is the general syrup left after the separation of cane-sugar or beet-sugar crystals from the concentrated juice. It is a dark coloured syrupy mass that still contains about 30 per cent of uncrystallizable sucrose and about 32 per cent of invert sugar—mixture of glucose and fructose. In India this by-product of sugar industry constitutes a suitable and cheap raw material for the manufacture of alcohol. The different steps involved in the manufacture are :

(*i*) **Dilution.** The molasses is diluted with water until a concentration of 8-10 per cent sugar is obtained in solution. This is acidified with a little sulphuric acid to retard bacterial growth. A nutritive solution like that of ammonium salts is added to act as food for the ferment if sufficient yeast food is not already present.

(*ii*) **Alcoholic Fermentation.** The dilute solution obtained above is taken in big fermentation tanks and some yeast is added (5% by volume of the liquid), the mixture is allowed to stand for a few days, and the temperature is maintained at about 330K. Fermentation sets in and the enzyme ***ivertase*** (present in yeast) converts sucrose into glucose and fructose which are further converted into ethanol by *zymase* (another enzyme present in east).

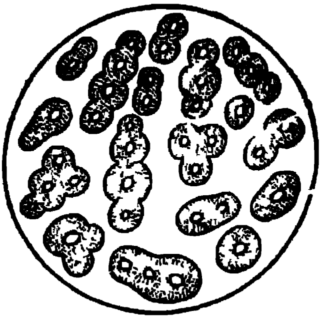


Fig. 18 1—Highly magnified yeart cells It is a single-cell living plant.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{in yeast}]{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{Glucose or Fructose}}{C_6H_{12}O_6} \xrightarrow[\text{in yeast}]{\text{Zymase}} \underset{\text{Ethanol}}{2C_2H_5OH} + 2CO_2$$

The fermentation is complete in about 3 days. The carbon dioxide is recovered and sold as a by-product

(*iii*) **Distillation.** The fermented liquor technically known **as wash** or **wort** contain 9-10 per cent enthanol, the rest being water and impurities. It is distilled in a specially designed continuous still called *Coffey still* (Fig 18 2) It consists of two tall fractionating columns called the *analyser* and the *rectifier* provided with perforated plates. It works on the counter-current principle as the steam and alcohol travel in opposite directions through the still.

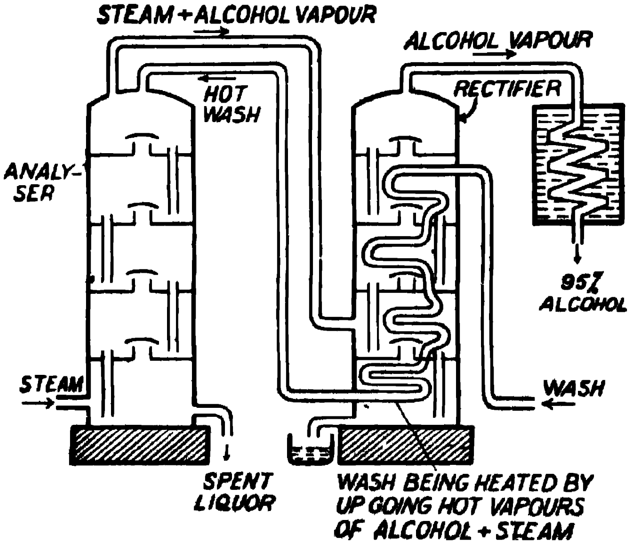


Fig. 18·2—Distillation of wash in a Coffey still.

Steam passes up the analyser and takes away the alcohol vapours from the down-coming dilute alcohol. The mixture leaves the analyser at the top and enters the rectifier near the base. Here it heats the *wort* flowing through the pipes on its way to the analyser. Most of the steam condenses and the alcohol vapours escaping near the top are condensed in the condenser. The distillate contains about 90 per cent alcohol and the residue left in the still is used as cattle feed.

(*iv*) **Rectification.** Alcohol obtained above contains in addition to water various other impurities which are removed by careful fractional distillation. Low boiling impurities, *e.g.*, acetaldehyde, distil over as *first fraction* while high boiling impurities—fusel oil, are collected as *last fraction*. The *middle fraction* is about 93-95 per cent alcohol called *Rectified spirit.*

In modern plants both distillation and rectification are done in one operation.

(B) FROM STARCH

Important starchy materials used are wheat, barley, rice, maize and potatoes. The conversion involves the following steps :

(1) **Conversion of Starch into Maltose.** Conversion of starch into maltose which is known as **saccharification** is carried out in the following three steps :

(*i*) *Malting.* Moist barley is allowed to germinate in dark rooms at 290K. Germinated barley called **Malt** is heated to 330K (to stop germination), crushed and extracted with water. The water extract called **Malt extract** contains the enzyme *diastase.*

(*ii*) *Mashing.* Starch is treated with superheated steam to break the cell walls and expose the starch inside which forms a paste-like mass called **Mash.**

(*iii*) *Hydrolysis.* Malt extract is added to the mash at 320-330K. Hydrolysis is complete in about half an hour's time.

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)_n}+nH_2O \xrightarrow[\text{malt extract}]{\text{Diastase in}} \underset{\text{Maltose}}{n\,C_{12}H_{22}O_{11}}$$

(2) **Alcoholic Fermentation.** The alcoholic fermentation of the maltose solution is carried out with yeast as in the manufacture of alcohol *from Molasses* (*see* page 2·142). Maltase present in yeast converts maltose into glucose. There is another enzyme zymase present in yeast. This converts glucose into ethanol.

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}}+H_2O \xrightarrow[\text{in yeast}]{\text{Maltase}} \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow[\text{in yeast}]{\text{Zymase}} \underset{\text{Ethanol}}{2C_2H_5OH} + 2CO_2$$

(3) **Distillation,** and (4) **Rectification** *are carried out as given in* (*A*) *before* (pages 2·142 and above.

25. By-products of Alcohol Industry.—The important by-products obtained during the manufacture of alcohol are :

(*i*) **Carbon dioxide.** Carbon dioxide is evolved during fermentation. It *is collected and sold as a by-product.*

(*ii*) **Acetaldehyde.** During rectification of alcohol the first runnings contain mainly acetaldehyde.

(*iii*) **Fusel oil.** The last runnings during rectification of alcohol consist mainly of high boiling alcohols, e.g., amyl alcohols. It is called *fusel oil* and is *used for the preparation of amyl alcohols or amyl acetate.*

(iv) ***Spent wash.*** *The residue, left in the still after distillation of wash, contains nitrogenous matter and is used as cattle feed.*

(*v*) ***Potassium hydrogen tartrate.*** *During fermentation of grape juice, a brown crust is formed at the top and is called* *argol.* This contains potassium hydrogen tartrate and is used for the preparation of tartaric acid and Rochelle salt.

26. Absolute Alcohol.—Alcohol mixed with water containing 95·6 per cent of alcohol gives a constant boiling mixture. Anhydrous or absolute alcohol cannot, therefore, be obtained by fractional distillation. Last traces of water are removed by treating the rectified spirit first with quicklime and distilling. Lime-distilled alcohol is then treated with anhydrous copper sulphate (white) until it does not turn blue or with metallic sodium followed by distillation.

Modern process for preparing absolute alcohol is by adding a small quantity of benzene to rectified spirit and distilling. The first fraction is the ternary mixture, *i.e.*, a constant boiling mixture (b.p. 337·8K) containing water, ethanol and benzene. After all the water has been removed, a binary mixture (b.p. 341·2K) containing ethanol and benzene distils over. When all the benzene has been removed, pure ethanol (b.p. 351·1K) distils over.

Ternary mixture on standing separates into two layers. Upper layer contains benzene and alcohol while the lower layer contains water and alcohol. The lower layer on fractional distillation gives rectified spirit. This along with the upper layer and the binary mixture are added to fresh rectified spirit and the process repeated.

27. Methylated Spirit.—Ordinary rectified spirit is called *industrial alcohol.* Methylated spirit is a mixture composed principally of ethanol (90 per cent) to which poisonous and nauseating materials like methanol, pyridine or mineral naphtha have been added. These materials are added to make sure that it will not be used for beverage purposes. The process is called *denaturing.* Pure alcohol is subjected to a heavy excise duty but denatured alcohol can be manufactured and sold duty free or with nominal duty for industrial use.

28. Power Alcohol.—With the advance of civilization the demand for petroleum has increased but petroleum resources of the world are still limited and are likely to be exhausted soon. A search for alternative fuels has, therefore, been going on since long. Manufacture of synthetic petrol was the first step in this direction and the use of industrial alcohol mixed with petrol and benzene is another step in the same direction. Absolute alcohol is miscible with petrol but industrial alcohol is not. In the presence of benzene, however, industrial alcohol mixes with petrol. *Alcohol thus used for the generation of power is called* **power alcohol.** India, with her meagre petroleum resources, can solve her petroleum problem by manufacturing more power alcohol from waste molasses—a by-product of sugar industry.

29. Alcoholic Beverages.—Liquors used for drinking purposes and containing alcohol as the principal intoxicating agent are called *alcoholic beverages.* These are prepared from different materials and contain different percentages of alcohol. There are two types of beverages—distilled and undistilled. Undistilled beverages prepared from grapes and other fruit juices are called *wines.* Wines are made stronger by addition of some rectified spirit and are called *fortified wines.*

Some common beverages are given below and contain colouring and flavouring materials besides a large proportion of water :

Distilled			**Undistilled**		
Name	*Source*	*%Alcohol*	*Name*	*Source*	*%Alcohol*
Whisky	Malt	35-40	**Beer**	**Barley**	**3-6**
Rum	Molasses	,,	**Cidar**	**Apples**	**2-6**
Brandy or **Cognac**	Grapes or Wine	,,	**Wine**	**Grapes**	**8-10**
Gin	Maize	,,	**Port and Sherry**	,,	14-20 (*fortified*)

30. **Alcoholometry.**—The strength of a sample of alcohol is found by determining its specific gravity and reading the percentage of alcohol against that value in the ready reference tables. To estimate the quantity of alcohol in a pharmaceutical preparation, 100 cm^3 of it is diluted with water and distilled till 100 cm^3 of the distillate is collected in a measuring flask. Specific gravity of the distillate is determined and the percentage of alcohol read against this value from ready reference table.

For excise purposes the percentage of alcohol is expressed in terms of proof spirit and tax levied on it. Proof spirit is a mixture of ethanol and water and contains 57·1% of the former by volume. A sample is called over- or underproof according as it is stronger or weaker than the proof spirit. For example, 10° underproof means that 100 volumes of sample contain as much of alcohol as 90 volumes of proof spirit. Similarly 10° overproof means that 100 volumes of sample contain as much alcohol as 110 volumes of proof spirit. *The determination of strength of alcohol is called* **alcoholometry.**

Formerly strength of alcohol was determined by pouring it over gun powder and then setting fire to it. The weakest possible alcohol which would allow gun-powder to catch fire was termed proof-spirit. Alcohol which would not allow gun-powder to burn was underproof while stronger solutions were called overproof.

UNSATURATED ALCOHOLS

31. Vinyl Alcohol, $CH_2{=}CHOH$.—Vinyl alcohol is unknown. All attempts to prepare this result in the formation of acetaldehyde. For example,

$$\underset{\text{Vinyl bromide}}{CH_2{=}CHBr} \xrightarrow{\text{AgOH}} \underset{\text{Hypothetical}}{[CH_2{=}CHOH]} \xrightarrow{\text{Isomerises}} \underset{\text{Acetaldehyde}}{CH_3{-}CHO}$$

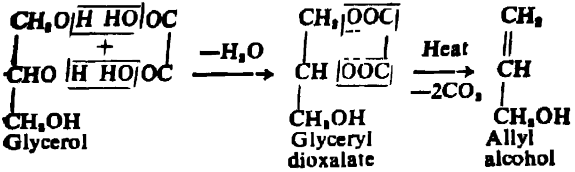
Many of the derivatives of this unknown alcohol have been prepared and are quite stable, *e.g.*, vinyl bromide, vinyl acetate, etc.

32. Allyl Alcohol, 2-Propene-1-ol, $CH_2=CH.CH_2OH$.—Allyl alcohol is prepared by the following methods :

(*i*) *By boiling allyl chloride or iodide with water.*

$$\underset{\text{Allyl halide}}{CH_2=CH.CH_2X}+H_2O \longrightarrow \underset{\text{Allyl alcohol}}{CH_2=CH.CH_2OH}+HX$$

(*ii*) *By heating glycerol with oxalic acid at 530K.*



$$\begin{array}{l} CH_2O\boxed{H\ HO}OC \\ |\qquad + \qquad | \\ CHO\ \boxed{H\ HO}OC \\ | \\ CH_2OH \end{array} \xrightarrow{-H_2O} \begin{array}{l} CH_2\boxed{OOC} \\ |\qquad\ \ | \\ CH\ \boxed{OOC} \\ | \\ CH_2OH \end{array} \xrightarrow[-2CO_2]{\text{Heat}} \begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2OH \end{array}$$

Glycerol Glyceryl dioxalate Allyl alcohol

Properties. It is a colourless pungent-smelling liquid (b.p. 370K) miscible with water, ethanol and ether in all proportions. In allyl alcohol are combined the properties of an unsaturated compound and a primary alcohol.

(*a*) **Properties of Unsaturated Compounds** :

(1) *Addition of hydrogen in presence of platinum.*

$$\underset{\text{Allyl alcohol}}{CH_2=CH.CH_2OH} + H_2 \xrightarrow{Pt} \underset{\text{1-Propanol}}{CH_3.CH_2.CH_2OH}$$

(2) *Addition of halogen* (*chlorine or bromine*).

$$\underset{\text{Allyl alcohol}}{CH_2=CH.CH_2OH} + Br_2 \longrightarrow \underset{\text{2, 3-Dibromo-1-propanol}}{CH_2Br.CHBr.CH_2OH}$$

(3) *Addition of halogen acids or hypohalous acids.* Allyl alcohol adds on halogen acid or hypohalous acids but the addition takes place contrary to Markownikoff's rule. This is due to the presence of hydroxyl group which exerts strong inductive effect. Here $-I$ effect of the hydroxyl group is stronger than the hyperconjugative effect (*see page* 1·101).

$$CH_2=CH.CH_2OH + HBr \longrightarrow \underset{\text{3-Bromo-1-propanol}}{CH_2BrCH_2.CH_2OH}$$

$$CH_2=CH.CH_2OH+H\overset{-}{O}\overset{+}{Cl} \longrightarrow \underset{\text{Glycerol }\beta\text{-monochlorohydrin}}{CH_2OH.CHCl.CH_2OH}$$

(4) *Oxidation.* With alkaline permanganate allyl alcohol is oxidised to glycerol.

$$CH_2=CH.CH_2OH+H_2O+[O] \longrightarrow \underset{\text{Glycerol}}{CH_2OH.CHOH.CH_2OH}$$

(*b*) **Properties of Alcoholic Group** :

(5) *With metallic sodium.* Hydrogen is liberated with sodium.

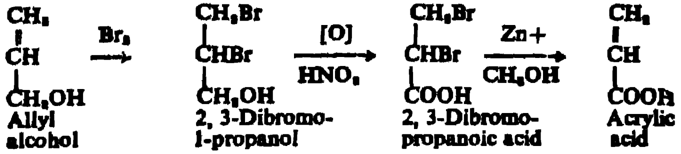
$$2CH_2=CH.CH_2OH+2Na \longrightarrow 2CH_2=CH.CH_2ONa+H_2$$

(6) *Esterification.* With organic and inorganic acids it gives esters.

$$CH_3CO\boxed{OH+H}OCH_2.CH=CH_2 \longrightarrow \underset{\text{Allyl acetate}}{CH_3COOCH_2.CH=CH_2}+H_2O$$

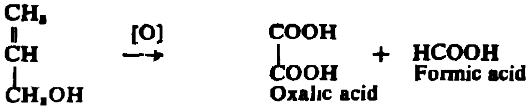
$$CH_2=CH.CH_2\boxed{OH + H}Cl \longrightarrow \underset{\text{Allyl chloride}}{CH_2=CH.CH_2Cl} + H_2O$$

(7) ***Oxidation of alcoholic group.*** If it is desired to oxidise only the alcoholic group in allyl alcohol, it is necessary to protect the double bond. This is done by addition of bromine before oxidising and its subsequent removal with zinc dust in methanolic solution.



$$\underset{\text{Allyl alcohol}}{\begin{array}{l}CH_2\\ \|\\ CH\\ |\\ CH_2OH\end{array}} \xrightarrow{Br_2} \underset{\text{2, 3-Dibromo-1-propanol}}{\begin{array}{l}CH_2Br\\ |\\ CHBr\\ |\\ CH_2OH\end{array}} \xrightarrow[HNO_3]{[O]} \underset{\text{2, 3-Dibromo-propanoic acid}}{\begin{array}{l}CH_2Br\\ |\\ CHBr\\ |\\ COOH\end{array}} \xrightarrow[CH_3OH]{Zn+} \underset{\text{Acrylic acid}}{\begin{array}{l}CH_2\\ \|\\ CH\\ |\\ COOH\end{array}}$$

On oxidation without previous protection of double bond, the chain gets ruptured at the position of the double bond in addition to oxidation of alcoholic group and a mixture of oxalic acid and formic acid is obtained.



$$\begin{array}{l}CH_2\\ \|\\ CH\\ |\\ CH_2OH\end{array} \xrightarrow{[O]} \underset{\text{Oxalic acid}}{\begin{array}{l}COOH\\ |\\ COOH\end{array}} + \underset{\text{Formic acid}}{HCOOH}$$

QUESTIONS

A. Essay Type :

1. State the reactions and the experimental conditions, if any, to obtain primary alcohols from the following compounds :

(*a*) an alkyl hydrogen sulphate, (*b*) an ester,

(*c*) a Grignard's reagent, (*d*) an amine.

(*Delhi B.Sc. Hons. Sub. 1976 Supp*)

2. What are alcohols and how are they classified ? What do you understand by primary, secondary and tertiary alcohols ? How will you distinguish between these classes of alcohols ? (*Jammu B.Sc. 1977 ; Delhi 1976*)

3. What are general methods for the preparation of alcohols ? (*Delhi B.Sc. 1976*)

4. How is methyl alcohol obtained on a large scale and by what chemical tests is it distinguished from ethyl alcohol ? (*Delhi B.Sc. 1976 Supp.*)

5. Give a brief account of the method of manufacture of absolute alcohol from a starchy material. Explain the chemical changes occurring at each stage. (*Jammu B.Sc. 1975, 77*)

6. Describe the manufacture of ethyl alcohol from molasses. How would you convert ethanol into acetaldehyde and ethyl acetate ? (*Delhi B.Sc. 1978 Supp., 76 ; Jammu 1975, 77*)

7. Illustrate Victor Meyer's and one more method for distinguishing primary, secondary and tertiary alcohols. (*Delhi B.Sc. 1981 ; Hons. Sub. 1976*)

8. Write short notes on : (*a*) Power alcohol. (*b*) Alcoholometry. (*c*) Proof spirit. (*d*) Absolute alcohol. (*e*) Denaturant.

9. On what evidence is *n*-propyl alcohol given the formula $CH_3.CH_2.CH_2OH$? How may *n*-propyl alcohol be converted into :

(*a*) *n*-Butyl alcohol ; (*b*) Ethyl alcohol ; (*c*) Isopropyl alcohol ?

10. How is allyl alcohol obtained from glycerol ? Give a brief account of what you know about allyl alcohol.

11. Indicate briefly the methods for the manufacture of isopropyl alcohol

12. What are primary, secondary and tertiary alcohols ? Starting with a Grignard reagent, how would you obtain each of them ? State what happens when the three types of alcohols are :

(*i*) Oxidised, and

(*ii*) Dehydrogenated catalytically. (*Punjab B.Sc. 1974*)

13. Starting from A how will you prepare B ?

	A	B
(*i*)	Isopropyl alcohol	2-Methyl-2-hexanol
(*ii*)	Secondary butyl alcohol	3-Methyl-3-pentanol.

(*Punjab B.Sc. 1976 Suppl.*)

14. How will you analyse alcohols with the help of Infrared and NMR spectra ? (*Punjab B.Sc. 1975*)

15. Indicate the absorption bands expected in the IR spectrum of $CH_3—CH_2OH$. (*G.N.D. B.Sc. 1976*)

16. Write a short note on the spectroscopic analysis of alcohols. (*Punjab B.Sc. 1976*)

B. Short Answer Type :

1. Give structural formulae and IUPAC names of the following organic compounds : (*i*) *sec*. Butyl alcohol; (*ii*) Diethylcarbinol ; (*iii*) Ethylmethyl-isopropylcarbinol ; (*iv*) isoamyl alcohol.

2. Write down the possible structural formulae and IUPAC names of various alcohols represented by the molecular formula $C_5H_{12}O$.

3. Give the reagents used and conditions employed for each step involved to bring about the following conversions :

(*i*) Acetaldehyde from ethanol,

(*ii*) Ethyl acetate from ethanol,

(*iii*) Methanol from ethanol and *vice versa*,

(*iv*) Primary alcohol from secondary alcohol and *vice versa*.

(*Delhi B.Sc. 1981 ; Rajasthan 1970*)

4. How are the following conversions effected :

(*i*) ethanol into propanol.

(*ii*) 1-propanol into 2-propanol ? (*Delhi B.Sc. Hons. Sub. 1977*)

5. Give chemical tests to distinguish between :

(*i*) *iso*-Propyl alcohol and *n*-propyl alcohol. (*Delhi B.Sc. 1976*)

(*ii*) *sec*-Butyl alcohol and isobutyl alcohol. (*Delhi B.Sc. Hons. 1976*)

6. Describe the reaction between ethanol and sulphuric acid under different conditions. (*Delhi B.Sc. 1976*)

7. Give two reactions of 1-propanol in which hydrogen atom of OH group reacts and two reactions in which hydroxyl group as a whole participates. How do you account for such a behaviour ? (*Delhi B.Sc. Hons. 1976*)

8. What products are formed on dehydration of 2-Butanol ? State the law which governs the elimination. (*Delhi B.Sc. Hons. 1976*)

9. Outline the stages involved in the following conversions :

(*i*) Isopropyl chloride to *n*-propyl chloride.

(*ii*) Propene to 2, 3-dimethylbutane.

(*iii*) Acetic acid to isopropyl alcohol. (*Delhi B.Sc. Hons. 1976*)

10. Give reasons to explain the fact that tertiary alcohols react less rapidly with metallic sodium but more rapidly with organic acids as compared to primary alcohols. (*Delhi B.Sc. Hons. 1976*)

11. Give equations to represent the oxidation of primary, secondary and tertiary alcohols. Name the products in each case. (*Punjabi B.Sc. 1976 Supp.*)

12. Lower members of alcohols are soluble in water. Explain why. (*Punjabi B.Sc. 1976 Supp.*)

13. Alcohols have higher boiling points than corresponding alkanes. Explain why. *(Punjab B.Sc. 1976 Supp.)*

14. Two bottles are supposed to contain chloroform and allyl alcohol. How will you establish their identity ? Give one test in each case. *(Delhi B.Sc. Hons. 1976)*

15. Two unlabelled bottles contain chloroform and methanol. How would you identify them ? Give one test in each case. *(Delhi B.Sc. Hons. Sub. 197')*

16. Write equations for the reactions between :

(*a*) Sodium amalgam and water+(*i*) acetyl chloride ; (*ii*) acetaldehyde (*iii*) acetone.

(*b*) Methylmagnesium iodide+(*i*) acetyl chloride : (*ii*) acetaldehyde and (*iii*) acetone.

(*c*) Methanol, +(*i*) sodium ; (*ii*) acetyl chloride ; (*iii*) ethylmagnesium iodide ; (*iv*) hydriodic acid ; (*v*) PCl$_5$ or PCl$_3$;

(*d*) Allyl alcohol+(*i*) H$_2$; (*ii*) Br$_2$, (*iii*) HBr ; (*iv*) HOCl ; (*v*) alkaline permanganate ; (*vi*) Na ; (*vii*) acetic acid ; (*viii*) Hydrochloric acid ;

(*ix*) HNO$_3$ (with and without protecting the double bond).

17. Discuss the hydrogen bonding in alcohols. *(Punjabi B.Sc. 1976)*

18. What is protonation of alcohols due to ? What different kinds of reactions protonated ethanol might undergo ?

19. Show how would you utilize hydroboration-oxidation procedure to prepare each of the following alcohols :

(*a*) 1-Hexanol (*b*) 3, 3-Diemethyl-1-butanol.

20. How would you prepare each of the following alcohols by acid-catalysed hydration of the appropriate alkene.

(*i*) 2-Pentanol (*ii*) Cyclopentanol (*iii*) *tert*-Butyl alcohol

21. Allyl alcohol, CH$_2$=CH—CH$_2$—OH, reacts immediately with Lucas reagent, although it is a primary alcohol. Explain why.

22. Acid catalysed hydration of 3,3 dimethyl-1-butene give 2,3 dimethyl-2-butanol as the major product. How can you account for this ?

23. Show how you might employ the oxymercuration-demercuration method for preparing each one of the following alcohols :

(*i*) 2-Pentanol (*ii*) Methylcyclohexanol

(*iii*) 2,4,4-Trimethyl-2-pentanol.

24. Show how you might prepare 2-Methyl-2-butanol through a Grignard synethesis in two different ways.

25. (*a*) Describe (in outlines only) the manufacture of ethyl alcohol from molasses. *(Delhi B.Sc. 1978 Supp.)*

26. How does ethanol react with the following :

(*i*) Conc H$_2$SO$_4$, (*ii*) HI. (*iii*) reduced copper heated to 570K. *(Delhi B.Sc. 1978 Supp.)*

27. How is ethyl alcohol converted into ethylene and ether ? *(Delhi B.Sc. 1978 Supp.)*

28. Write a short note on fermentation. *(Delhi B.Sc. Hons. 1978)*

29. How will you convert the following ?

(*i*) Primary alcohol into tertiary alcohol.

(*ii*) $n\text{-C}_3\text{H}_7\text{COOH} \xrightarrow{?} n\text{-C}_4\text{H}_9\text{OH}$ *(Delhi B.Sc. Hons. 1978)*

30. Give the mechanism of acid-catalysed dyhydration of alcohols.
(Delhi B.Sc. 1981)

31. State the action of the following on ethyl alcohol : PCl_5, (*ii*) H_2SO_4 (*iii*) CH_3COOH (*iv*) Bleaching powder. *(Delhi B.Sc. Hons. Sub. 1981)*

C. Problems :

1. Derive the structure of an organic compound from the following data ;

(*a*) On bromination 2·9 g of the compound yields 10·9 g of the bromo-derivative ($C_3H_6OBr_2$).

(*b*) On treatment with hydrochloric acid, 2·9 g of the compound yields 3·83 g of the chloro-derivative (C_3H_5Cl).

(*c*) On reduction, the compound yields *n*-propyl alcohol.

(*d*) On treatment of the compound with sodium, hydrogen is evolved.

(*e*) The molecular formula of the compound is C_3H_6O.

2. An organic compound A containing 62·07% carbon and 10·35% hydrogen, was obtained by the oxidation of a compound B containing 60% carbon and 13·33% hydrogen and vapour density 30. The compound A on treatment with PCl_5 gave a compound C the vapour density of which was 56·5. On oxidation A gave an acid D, the silver salt of which contained 51·5% silver. Write the structural formulae of A, B, C and D.

3. An alcohol $C_5H_{11}OH$ gives a ketone on oxidation. On dehydration the alcohol gives alkene. The alkene on oxidation give acetone and acetic acid. Assign structures to the alcohol and the reaction products mentioned above.

4. An organic compound C_3H_6O (A) may be reduced to C_3H_8O (B), which further reacts with thionyl chloride to give C_3H_7Cl (C). The Grignard reagent obtained from C reacts with A to produce $C_6H_{14}O$ (D) which gives on oxidation the ketone $C_6H_{12}O$ (E). A does not give iodoform reaction. Identify the compounds A to E.

5. An organic compound C_2H_6O (A) gives on oxidation C_2H_4O (B); which on further oxidation with iodine and caustic soda yields the salt of $C_2H_4O_2$ (C). B reacts with ethylmagnesium iodide to give $C_4H_{10}O$ (D). Identify the compounds A to D.

6. A primary alcohol $C_4H_{10}O$ (A) reacts with thionyl chloride to give C_4H_9Cl (B). On suitable treatment both A and B give C_4H_8 (C) which reacts with hydrochloric acid to give D, an isomer of B. The compound C on oxidation gives $C_3H_6O_2$ (E) together with carbon dioxide and water.

Identify the compounds A to E.

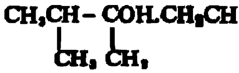
7. An organic compound C_3H_6O (A) gives on oxidation $C_3H_6O_2$ (B). A reacts with ethylmagnesium iodide to give $C_5H_{12}O$ (C) which on dehydration gives C_5H_{10} (D). With acid permanganate D is oxidised to B and $C_2H_4O_2$ (E).

Identify the compounds A to E.

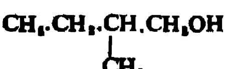
ANSWERS

B. 1. (*i*) $CH_3CH_2.CHOH.CH_3$ (*2-Butanol*)

(*ii*) $CH_3CH_2.CHOH.CH_2CH_3$ (*3-Pentanol*)

(*iii*)

$CH_3\underset{CH_3}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{C}}OH.CH_2CH_3$ (*2,3-Dimethyl-3-Pentanol*)

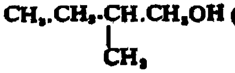
(*iv*)

$CH_3.\underset{CH_3}{\underset{|}{CH}}.CH_2.CH_2OH$
or

$CH_3.CH_2.\underset{CH_3}{\underset{|}{CH}}.CH_2OH$

(*3-Methyl-1-butanol*) (*2 Methyl-1.butanol*)

2. (*i*) $CH_3.CH_2.CH_2.CH_2CH_2OH$ (*1-Pentanol*)

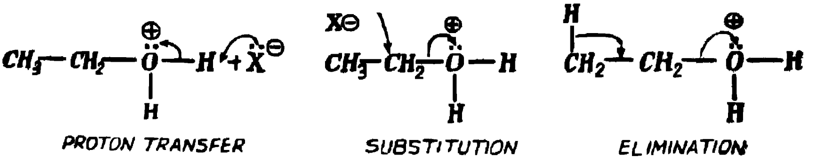
(*ii*) $(CH_3)_2CH.CH_2.CH_2OH$ (*3-Methyl-1-butanol*)

(*iii*)

$CH_3.CH_2.\underset{CH_3}{\underset{|}{CH}}.CH_2OH$ (*2-Methyl-1-butanol*)

(*iv*) $(CH_3)_3C.CH_2OH$ (*2, 2-Dimethyl-1-propanol*)
(*v*) $CH_3.CH_2.CH_2.CHOH.CH_3$ (*2-Pentanol*)
(*vi*) $CH_3.CH_2.CHOH.CH_2CH_3$ (*3-Pentanol*)
(*vii*) $(CH_3)_2COH.CH_2.CH_3$ (*2-Methyl-2-butanol*)
(*viii*) $(CH_3)_2CH.CHOH.CH_3$ (*3-Methyl-2-butanol*)

18. **Alcohols behave as nucleophiles due to the presence of lone pairs on oxygen atom.**

Different kinds of reactions :



C. 1. $CH_2{=}CH.CH_2OH$ (*Allyl alcohol*)

2. $$\underset{\text{n-Propyl alcohol (B)}}{CH_3.CH_2.CH_2OH} \xrightarrow{[O]} \underset{\text{Propionaldehyde (A)}}{C_2H_5CHO} \xrightarrow{[O]} \underset{\text{Propionic acid (C)}}{C_2H_5COOH}$$

$$C_2H_5CHO \xrightarrow{PCl_5} \underset{\text{Propylidene chloride (D)}}{C_2H_5CHCl_2}$$

3. $$\underset{\substack{\text{3-Methyl-2-butanol}\\ (\textit{Alcohol}, C_5H_{11}OH)}}{(CH_3)_2CH.CHOH.CH_3} \xrightarrow{[O]} \underset{\substack{\text{3-Methyl-2-butanone}\\ (\textit{Ketone})}}{(CH_3)_2CH.COCH_3}$$

$$\downarrow -H_2O$$

$$\underset{\substack{\text{2-Methyl-2-butene}\\ (\textit{Alkene})}}{(CH_3)_2C{=}CH.CH_3} \xrightarrow{[O]} \underset{\text{Acetone}}{\substack{CH_3\\ CH_3}{>}C{=}O} + CH_3COOH$$

4. A is C_2H_5CHO (*Propionaldehyde*)
B is $CH_3.CH_2.CH_2OH$ (*n-Propyl alcohol*)
C is $CH_3.CH_2.CH_2Cl$ (*n-Propyl chloride*)
D is $CH_3CH_2CH_2.CHOH.C_2H_5$ (*3-Hexanol*)
E is $CH_3.CH_2.CH_2CO.C_2H_5$ (*3-Hexanone*)

5. A is $(CH_3)_2CHOH$ (*2-Propanol*)
B is $CH_3CO.CH_3$ (*Acetone*)
C is CH_3COOH (*Acetic acid*)
D is $(CH_3)_2COH.C_2H_5$ (*2-Methyl-2-butanol*)

6. A is $CH_3.CH_2.CH_2.CH_2OH$ (*1-Butanol*)
B is $CH_3.CH_2.CH_2CH_2Cl$ (*1-Chlorobutane*)
C is $CH_3.CH_2.CH{=}CH_2$ (*1-Butene*)
D is $CH_3.CH_2CHCl.CH_3$ (*2-Chlorobutane*)
E is $CH_3.CH_2.COOH$ (*Propanoic acid*)

7. A is $CH_3.CH_2.CHO$ (*Propionaldehyde or Propanal*)
B is $CH_3.CH_2.COOH$ (*Propionic acid*)
C is $CH_3.CH_2.CHOH.CH_2.CH_3$ (*3-Pentanol*)
D is $CH_3.CH_2.CH{=}CH.CH_3$ (*2-Pentene*)
E is CH_3COOH (*Ethanoic acid*)

19

Dihydric and Trihydric Alcohols

1. **Dihydric Alcohols.**—Alcohols containing two hydroxyl groups are called *dihydric alcohols or glycols.* The two hydroxyl groups are attached to two different carbon atoms as two hydroxyl groups attached to the same carbon atom make the compound unstable and water is eliminated (*see* page 2·122).

Glycols are classified as α, β-, γ-, ... glycols according to the relative positions of the two hydroxyl groups. 1, 2-glycol is termed α-, 1, 3 is called β-, 1, 4 is known as γ-, and so on.

2. **Nomenclature.**—The common names of the α-glycols are derived from the corresponding olefins from which these may be prepared by direct hydroxylation. According to the IUPAC system of nomenclature, the class suffix is *-diol* and these are considered as derivatives of alkanes. Thus IUPAC name is *alkanediol.* Names of some individual members are :

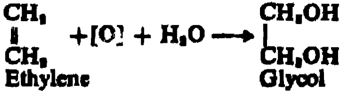
Formula	*Common name*	*IUPAC name*
$CH_2OH.CH_2OH$	Ethylene glycol or Glycol	1,2-Ethanediol
$CH_3CHOH.CH_2OH$	Propylene glycol	1,2-Propanediol
$CH_3\underset{\underset{CH_3}{\vert}}{C}OH.CH_2OH$	Isobutylene glycol	2-Methyl-1, 2-propanediol

β-, γ-, ... glycols are named as the corresponding polymethylene glycols. For example,

Formula	*Common name*	*IUPAC name*
$CH_2OH.CH_2.CH_2OH$	Trimethylene glycol	1, 3-Propanediol
$CH_2OH.(CH_2)_3.CH_2OH$	Pentamethylene glycol	1, 5-Pentanediol

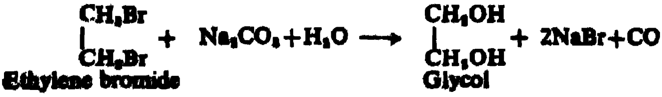
3. **Ethylene Glycol, Glycol** (*1, 2-Ethanediol*).—Glycol, $CH_2OH.CH_2OH$ is the simplest and the most important dihydric alcohol and may be prepared as follows :

(*i*) *By passing ethylene into cold dilute alkaline permanganate solution.* Ethylene is oxidised to glycol.



$$\underset{\text{Ethylene}}{\begin{matrix}CH_2\\ \Vert\\ CH_2\end{matrix}} + [O] + H_2O \longrightarrow \underset{\text{Glycol}}{\begin{matrix}CH_2OH\\ \vert\\ CH_2OH\end{matrix}}$$

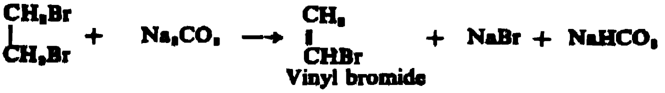
(*ii*) *By hydrolysis of ethylene bromide by boiling* (*under reflux*) *with aqueous sodium carbonate solution* (**Laboratory method**).



$$\underset{\text{Ethylene bromide}}{\begin{matrix}CH_2Br\\ \vert\\ CH_2Br\end{matrix}} + Na_2CO_3 + H_2O \longrightarrow \underset{\text{Glycol}}{\begin{matrix}CH_2OH\\ \vert\\ CH_2OH\end{matrix}} + 2NaBr + CO_2 \qquad (f.g.)$$

The reaction mixture is refluxed till oily globules of ethylene bromide disappear. The resulting solution is evaporated on a water bath. Glycol is extracted from the semi-solid residue with ether-alcohol mixture. Glycol is recovered from the solution by distillation.

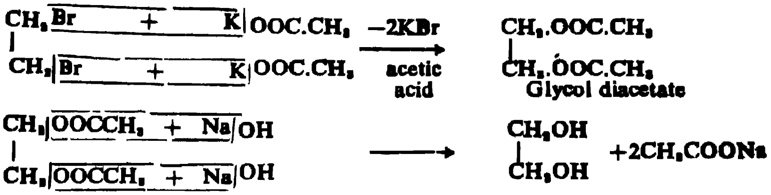
Some ethylene bromide is converted into vinyl bromide. The yield is, therefore, low.



$$\begin{array}{l} CH_2Br \\ | \\ CH_2Br \end{array} + Na_2CO_3 \longrightarrow \begin{array}{l} CH_2 \\ \| \\ CHBr \end{array} + NaBr + NaHCO_3$$

Vinyl bromide

If caustic soda (*aqueous*) is used in place of sodium carbonate vinyl bromide is again obtained as by-product. The best yield of glycol (83-84%) can be obtained by heating ethylene bromide with potassium acetate in glacial acetic acid. Glycol diacetate thus obtained is hydrolysed with dilute caustic soda solution.

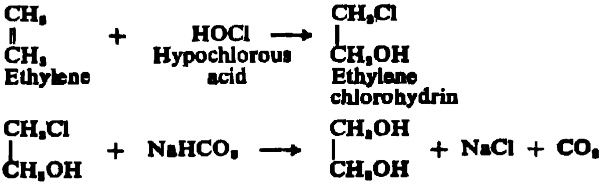


$$\begin{array}{l} CH_2Br + K\,OOC.CH_3 \\ | \\ CH_2Br + K\,OOC.CH_3 \end{array} \xrightarrow[\text{acetic acid}]{-2KBr} \begin{array}{l} CH_2.OOC.CH_3 \\ | \\ CH_2.OOC.CH_3 \end{array}$$

Glycol diacetate

$$\begin{array}{l} CH_2OOCCH_3 + Na\,OH \\ | \\ CH_2OOCCH_3 + Na\,OH \end{array} \longrightarrow \begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} + 2CH_3COONa$$

(*iii*) **Glycol is prepared industrially** *by passing ethylene into hypochlorous acid and hydrolysing the ethylene chlorohydrin formed by boiling with aqueous bicarbonate.*

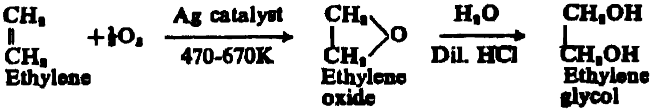


$$\begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array} + \underset{\text{Hypochlorous acid}}{HOCl} \longrightarrow \begin{array}{l} CH_2Cl \\ | \\ CH_2OH \end{array}$$

Ethylene — Ethylene chlorohydrin

$$\begin{array}{l} CH_2Cl \\ | \\ CH_2OH \end{array} + NaHCO_3 \longrightarrow \begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} + NaCl + CO_2$$

(*iv*) *By hydrolysis of ethylene oxide with dilute hydrochloric acid* (**Industrial method**). Ethylene oxide is prepared by passing a mixture of ethylene and air under pressure over silver catalyst at 470-670K.



$$\begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array} + \tfrac{1}{2}O_2 \xrightarrow[470\text{-}670K]{\text{Ag catalyst}} \begin{array}{l} CH_2 \\ | \\ CH_2 \end{array}\!\!>O \xrightarrow[\text{Dil. HCl}]{H_2O} \begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array}$$

Ethylene — Ethylene oxide — Ethylene glycol

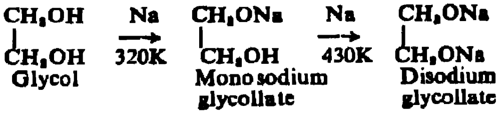
4. Properties of Glycol.—

(*a*) **Physical.** Glycol is a colourless, syrupy liquid (m.p. 261·5K ; b.p. 400K) sweet in taste. The sweet taste is indicated by the prefix *glyco* (Greek, *Glukus*=sweet). It is miscible with water and ethanol in all proportions but is insoluble in ether.

Due to its two sites for hydrogen bonding per molecule glycol has a high boiling point and is also highly soluble in water.

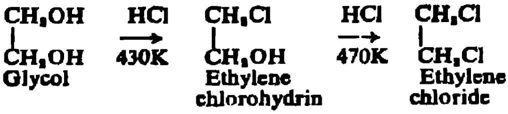
(*b*) **Chemical.** There are two primary alcoholic groups present in glycol. Its reactions are, therefore, as expected of a monohydric primary alcohol. The two primary alcoholic groups, however, are not equally reactive ; one group always completely reacts before the other is attacked. Further the two groups can be made to undergo two different types of reactions.

(1) *Action of sodium.* Monosodium glycollate is obtained when glycol is treated with sodium at 320K while disodium derivative is obtained at 430K.



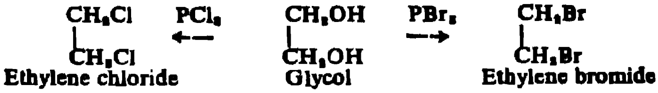
$$\underset{\text{Glycol}}{\begin{array}{l}CH_2OH\\|\\CH_2OH\end{array}}\xrightarrow[320K]{Na}\underset{\text{Monosodium glycollate}}{\begin{array}{l}CH_2ONa\\|\\CH_2OH\end{array}}\xrightarrow[430K]{Na}\underset{\text{Disodium glycollate}}{\begin{array}{l}CH_2ONa\\|\\CH_2ONa\end{array}}$$

(2) *Action of hydrogen chloride.* Hydrogen chloride converts glycol into ethylene chlorohydrin at 430K whereas ethylene chloride is formed at 470K.



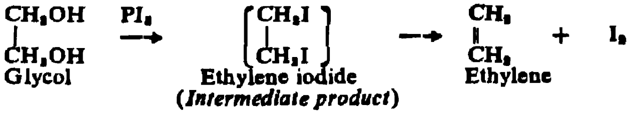
$$\underset{\text{Glycol}}{\begin{array}{l}CH_2OH\\|\\CH_2OH\end{array}}\xrightarrow[430K]{HCl}\underset{\text{Ethylene chlorohydrin}}{\begin{array}{l}CH_2Cl\\|\\CH_2OH\end{array}}\xrightarrow[470K]{HCl}\underset{\text{Ethylene chloride}}{\begin{array}{l}CH_2Cl\\|\\CH_2Cl\end{array}}$$

(3) *Action of phosphorus halides.* On treating glycol with phosphorus trichloride or phosphorus tribromide, the corresponding ethylene halide is obtained.



$$\underset{\text{Ethylene chloride}}{\begin{array}{l}CH_2Cl\\|\\CH_2Cl\end{array}}\xleftarrow{PCl_3}\underset{\text{Glycol}}{\begin{array}{l}CH_2OH\\|\\CH_2OH\end{array}}\xrightarrow{PBr_3}\underset{\text{Ethylene bromide}}{\begin{array}{l}CH_2Br\\|\\CH_2Br\end{array}}$$

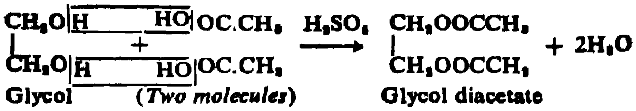
With phosphorus triiodide, however, glycol gives ethylene. Ethylene iodide which is formed as an intermediate product, readily loses a molecule of iodine to form ethylene.



$$\underset{\text{Glycol}}{\begin{array}{l}CH_2OH\\|\\CH_2OH\end{array}}\xrightarrow{PI_3}\underset{\substack{\text{Ethylene iodide}\\(\textit{Intermediate product})}}{\left[\begin{array}{l}CH_2I\\|\\CH_2I\end{array}\right]}\longrightarrow\underset{\text{Ethylene}}{\begin{array}{l}CH_2\\\|\\CH_2\end{array}}+I_2$$

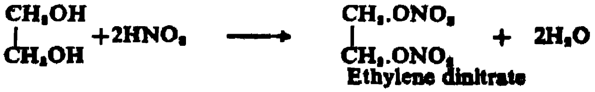
(4) *Action of acids.* Organic acids or inorganic oxy-acids give mono- or di-ester with glycol depending upon their relative amounts. For example :

(*i*) Glycol diacetate is obtained with acetic acid in the presence of a little sulphuric acid as catalyst.



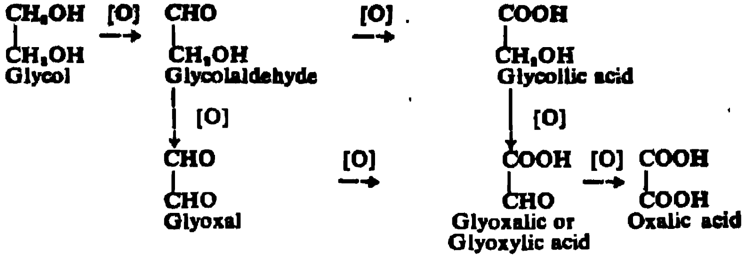
$$\underset{\text{Glycol}}{\begin{array}{l}CH_2O\\|\\CH_2O\end{array}}\!\!\underset{(\textit{Two molecules})}{\boxed{\begin{array}{lcr}H & + & HO\\H & & HO\end{array}}}\!\!\begin{array}{l}OC.CH_3\\ \\OC.CH_3\end{array}\xrightarrow{H_2SO_4}\underset{\text{Glycol diacetate}}{\begin{array}{l}CH_2OOCCH_3\\|\\CH_2OOCCH_3\end{array}}+2H_2O$$

(*ii*) With a mixture of conc. nitric acid and conc. sulphuric acid glycol gives ethylene dinitrate.

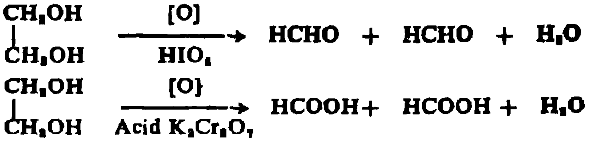


$$\begin{array}{l}CH_2OH\\|\\CH_2OH\end{array}+2HNO_3\longrightarrow\underset{\text{Ethylene dinitrate}}{\begin{array}{l}CH_2.ONO_2\\|\\CH_2.ONO_2\end{array}}+2H_2O$$

(5) *Oxidation.* When glycol is oxidised with nitric acid, all theoretically possible oxidation products are obtained though in very poor yields except glycollic and oxalic acids which may be readily isolated in good yield.



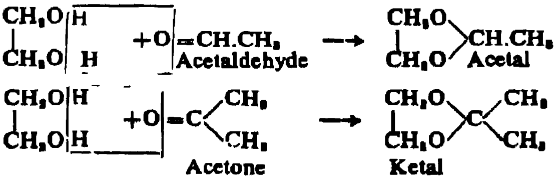
Oxidation of glycol with acid permanganate, acid dichromate, and tetra-acetate—$(CH_3COO)_4$ Pb or periodic acid (HIO_4), results in the fission of the carbon-carbon bond.



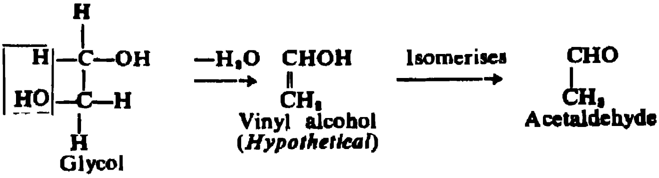
$$\begin{array}{l}CH_2OH\\|\\CH_2OH\end{array}\xrightarrow[HIO_4]{[O]} HCHO + HCHO + H_2O$$

$$\begin{array}{l}CH_2OH\\|\\CH_2OH\end{array}\xrightarrow[\text{Acid } K_2Cr_2O_7]{[O]} HCOOH + HCOOH + H_2O$$

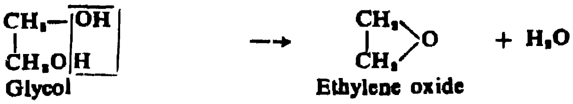
(6) *Condensation with aldehydes or ketones.* Glycol condenses with aldehydes or ketones in the presence of acid to give cyclic acetals or cyclic ketals respectively.



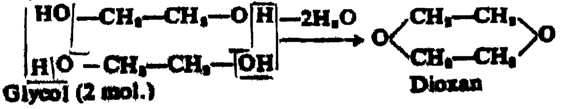
(7) *Dehydration.* (*i*) With dehydrating agents like sulphuric acid or zinc chloride glycol is converted into acetaldehyde.



(*ii*) When heated above 770K, glycol yields ethylene oxide.



(*iii*) It gives dioxan (an industrial solvent) when distilled with a little sulphuric acid or concentrated phosphoric acid.



5. Uses.—(*i*) As an antifreeze* in automobile radiators.

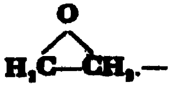
(*ii*) As a solvent and as a preservative.

(*iii*) Its dinitrate is used as an explosive with trinitroglycerine.

(*iv*) As a substitute for glycerine in commerce but not in medicine as it is readily oxidises to oxalic acid (poisonous).

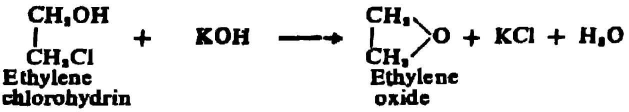
(*v*) As a cooling agent in aeroplanes instead of water.

6. Ethylene Oxide (*epoxyethane*),



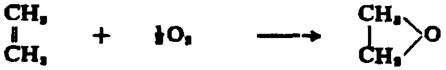
Preparation. Ethylene oxide may be prepared :

(*i*) *By distilling ethylene chlorohydrin with concentrated potassium hydroxide solution.*

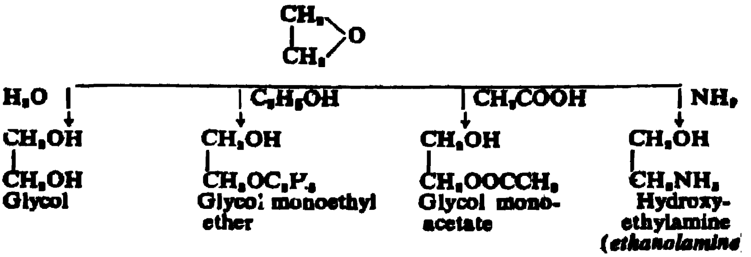


In commerce calcium hydroxide (cheaper alkali) is used in place of caustic potash.

(*ii*) *By passing a mixture of ethylene and air under pressure over silver catalyst at 500-700K (Industrial method).*



Properties. Ethylene oxide is a colourless gas (b.p. 380K), soluble in water, ethanol and ether. Its chemical properties may be summarized as follows :



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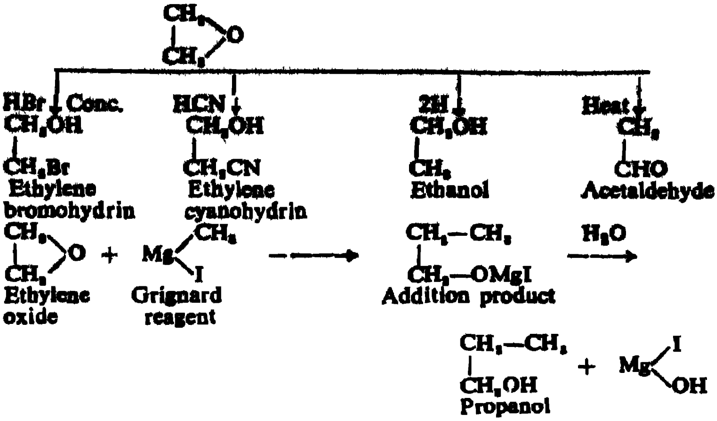
* Water used for cooling in a car radiator is likely to freeze if the temperature falls below 273K. Water expands on freezing and this may cause the engine block to burst. It is, therefore, necessary to mix something with water to lower its freezing point.

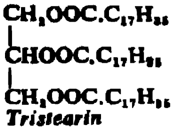
Due to its high solubility and low volatility, glycol is used for this purpose and is termed antifreeze. Water containing 40% glycol freezes at about 224K, *i.e.*, 49 degrees below its normal freezing point.

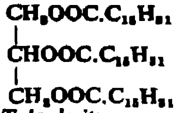


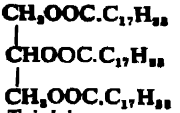
Uses. (*i*) Ethylene oxide mixed with 10% CO_2 is an excellent fumigant for tobacco, grain, etc., and is sold under the trade name T-gas or Etox.

(*ii*) It is also used in the manufacture of methyl and ethyl cellosolves (*useful solvents*).

7. **Trihydric Alcohols, $C_nH_{2n-1}(OH)$.**—The only important trihydric alcohol is glycerol, 1,2,3-propanetriol, commonly known as glycerine—$CH_2OH.CHOH.CH_2OH$. It is present in almost all the animal and vegetable oil and fats as glycerides (glyceryl esters) of mainly palmitic acid ($C_{15}H_{31}COOH$), stearic acid ($C_{17}H_{35}COOH$), and oleic acid ($C_{17}H_{33}COOH$).


Tristearin

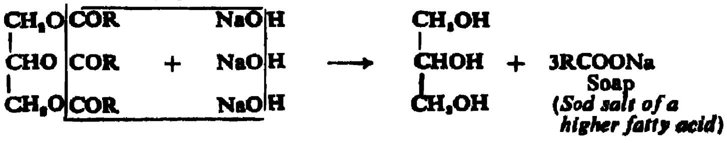

Tripalmitin


Triolein

8. **Manufacture of Glycerol.**—Different methods used for industrial preparation of glycerol are :

(1) **By the hydrolysis of fats and oils (the glycerides of Higher fatty acids).** The hydrolysis is carried out for the manufacture of soap or higher fatty acids needed for the manufacture of candles. In both these cases glycerol is obtained as a valuable by-product.

(*a*) *During Soap Mannfacture,* the hydrolysis is effected with an alkali solution (*Lye*).



After the separation of soap the *spent lye* or *sweet lye* is treated for the recovery of glycerol. It contains free alkali, some soluble soap, sodium chloride (used during salting out of soap), suspended impurities and water.

It is taken into a *settling tank* where most of the suspended matter settles down. The decanted solution is transferred to a treating tank and treated with aluminium sulphate which precipitates free alkali as aluminium hydroxide and soluble soap as aluminium soap. This is filtered by passing through a *filter press* and taken into the *storage tank*. The dilute solution is then concentrated under reduced pressure in *concentration pan* wherein low pressure steam is used as the heating material. As the solution concentrates, sodium chloride separates and collects in the salt boxes below.

The concentrated solution is next decolorised with animal charcoal and distilled in a *vacuum pan* wherein superheated steam is used for heating. The 30 per cent glycerol obtained may be redistilled.

Distillation under reduced pressure is necessary since glycerol decomposes on heating at much below its boiling point.

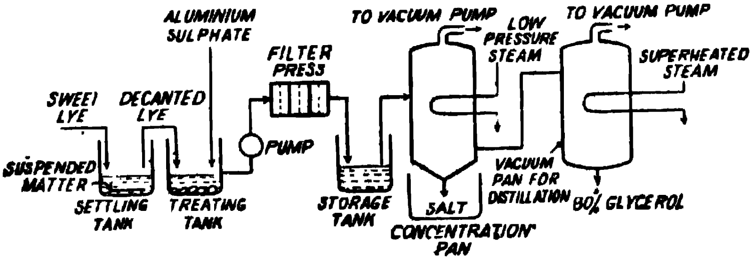


Fig. 19·1—Flow sheet for the recovery of glycerol from Spent lye or Sweet lye.

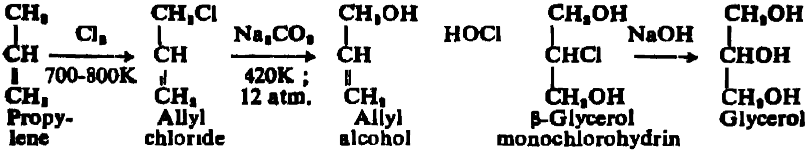
(*b*) *During Candle Manufacture*, the hydrolysis is carried out with superheated steam under pressure in presence of a little sulphuric acid.

$$\begin{array}{llll}
CH_2O|\overline{COR \quad + \quad HO}|H & & CH_2OH & \\
\quad | & & \quad | & \\
CHO\ |\overline{COR \quad + \quad HO}|H & \longrightarrow & CHOH & + \quad 3RCOOH \\
\quad | & & \quad | & \quad \text{Higher fatty acid} \\
CH_2O|\overline{COR \quad + \quad HO}|H & & CH_2OH & \quad (\textit{Waxy solid used in} \\
\text{Fat or oil} & & \text{Glycerol} & \quad \textit{candle manufacture})
\end{array}$$

The mixture is distilled when fatty acid is left behind as residue. The distillate (*sweet water*) contains water and glycerol along with a little of volatile fatty acids. It is neutralized with some sodium carbonate and steam distilled. Volatile fatty acids form non-volatile sodium salts and are left behind as residue while a dilute solution of glycerol distils over. The dilute solution so obtained is concentrated under vacuum and purified as described above.

(2) **By Fermentation of Sugar.** Glycerol is present as an impurity in alcohol produced by fermentation of molasses. Its yield increases from 3 to 20-25 per cent when fermentation is carried out in presence of sodium sulphite added in suitable proportion. Hence fermentation occurs in an alkaline medium provided by the hydrolysis of sodium sulphite. This results in greater yield of glycerol which is separated by fractional distillation.

(3) **Synthetic Glycerol.** Glycerol is now also produced synthetically as follows :

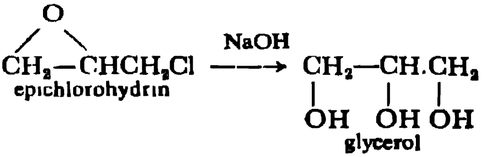

CH₃ CH CH₃ Propylene
Cl₂ 700-800K
CH₂Cl CH CH₂ Allyl chloride
Na₂CO₃ 420K ; 12 atm.
CH₂OH CH CH₂ Allyl alcohol
HOCl
CH₂OH CHCl CH₂OH β-Glycerol monochlorohydrin
NaOH
CH₂OH CHOH CH₂OH Glycerol

The starting material, propylene is obtained during the cracking of petroleum and constitutes about 30 per cent of the gases obtained.

Addition of hypochlorous acid to allyl alcohol takes place contrary to Markownikoff's rule. This is due to the presence of oxygen atom which exerts strong inductive effect. Here -I effect of the hydroxyl group is stronger than the hyperconjugative effect.

An alternative route for getting glycerol from allyl chloride tained above is :

$$ClCH_2CH{=}CH_2 \xrightarrow{HOCl} \left.\begin{matrix} ClCH_2CHOHCH_2Cl \\ + \\ ClCH_2CHClCH_2OH \end{matrix}\right\} CaO$$



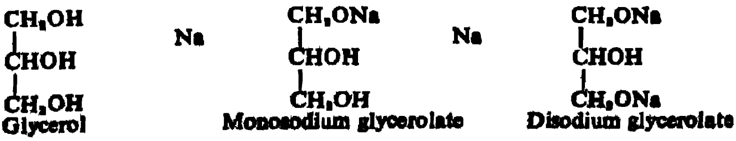
9. Properties of Glycerol.—

(*a*) **Physical.** Glycerol is a colourless, odourless, syrupy liquid (Sp. Gr. 1·265), sweet in taste. It is miscible with water and ethanol in all proportions but is almost insoluble in ether. Pure glycerol boils at 563K with slight decomposition and on cooling gives transparent crystals (m.p. 290K). It is very hygroscopic in nature.

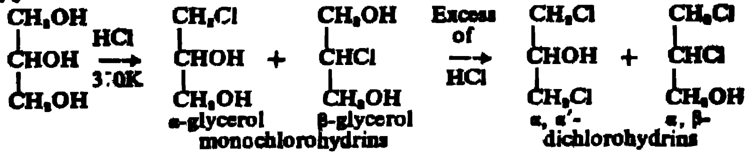
Due to the presence of three sites for hydrogen bonding, intermolecular forces are strong. This is responsible for its high boiling point and high viscosity (syrupy nature). Its high solubility is also due to the presence of three sites for hydrogen bonding with water.

(*b*) **Chemical.** Glycerol contains one secondary and two primary alcoholic groups, and it undergoes many of the reactions to be expected of these types of alcohols as given below :

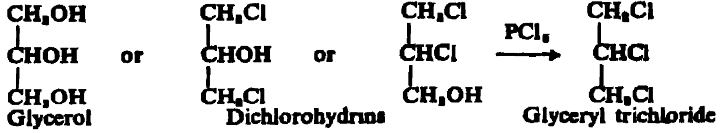
(*i*) *Action of Sodium.* When glycerol is treated with sodium, monosodium glycerolate is readily obtained and the disodium glycerolate less readily. The third, secondary alcoholic group is not ttacked at all.


CH₂OH CHOH CH₂OH Glycerol
Na
CH₂ONa CHOH CH₂OH Monosodium glycerolate
Na
CH₂ONa CHOH CH₂ONa Disodium glycerolate

(*ii*) ***Action with Hydrogen chloride.*** Glycerol reacts with gaseous hydrogen chloride at 370K to give both α- and β-glycerol monochlorohydrins, the former being about 66%. Continued action with hydrogen chloride taken in excess produces glycerol α : α′-dichlorohydrin, and α, β-dichlorohydrin, the former being about 55-57%.



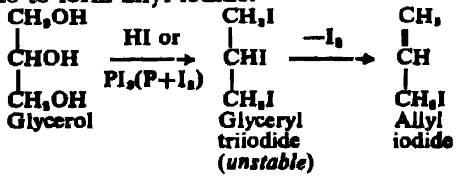
Glycerol itself or any of these chlorohydrins when treated with phosphorus pentachloride yields glyceryl trichloride.



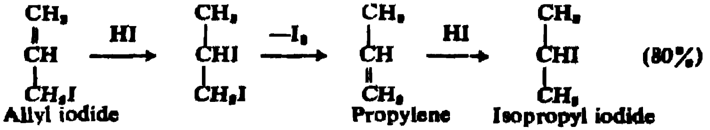
Hydrogen bromide and phosphorus tribromide react in the same way as hydrogen chloride given above.

(*iii*) *Action of Phosphorus triiodide.* When glycerol is treated with a *small amount of hydrogen iodide or phosphorus triiodide*, allyl iodide is the main product.

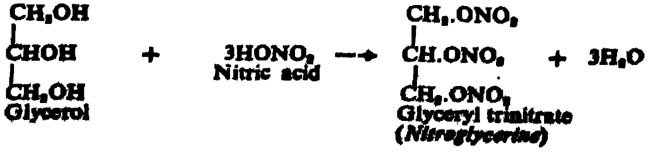
An unstable triiodide is formed as an intermediate product which loses iodine to form allyl iodide.



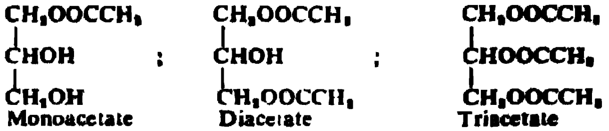
When a large amount of phosphorus triiodide is used allyl iodide further reacts to give isopropyl iodide which is the main product.



(*iv*) *Action of Acids. On treating glycerol with monocarboxylic* acids, mono-, di- or tri-esters are obtained depending upon the amount of acid used. High temperature and an excess of acid favour formation of the tri-ester. For example, with a well-cooled mixture of concentrated sulphuric acid and fuming nitric acid, nitroglycerine is formed.



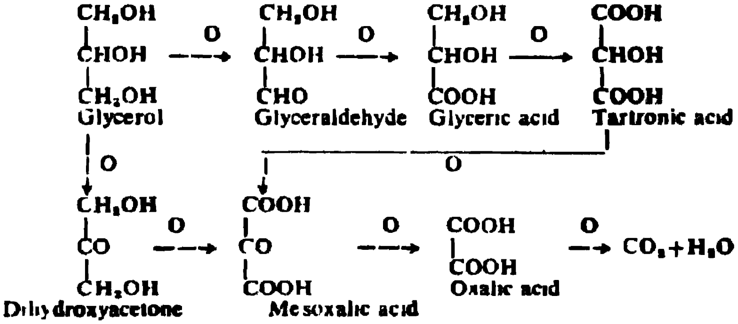
Similarly with acetic acid or acetic anhydride, mono-, di- and tri-acetates are obtained.



$$\begin{array}{c} CH_2OOCCH_3 \\ | \\ CHOH \\ | \\ CH_2OH \end{array} ; \quad \begin{array}{c} CH_2OOCCH_3 \\ | \\ CHOH \\ | \\ CH_2OOCCH_3 \end{array} ; \quad \begin{array}{c} CH_2OOCCH_3 \\ | \\ CHOOCCH_3 \\ | \\ CH_2OOCCH_3 \end{array}$$

Monoacetate; Diacetate; Triacetate

(*v*) *Oxidation*. Theoretically glycerol can give rise to a large variety of oxidation products. The actual products obtained, in practice, however, depend on the nature of oxidising agent.

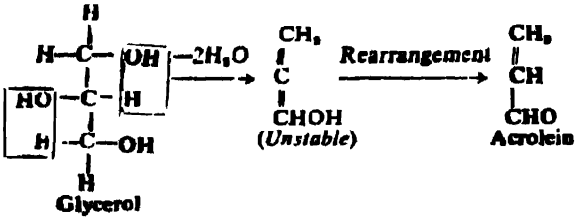


Dilute nitric acid oxidises it to glyceric and tartronic acids while concentrated nitric acid produces mainly glyceric acid (yield =83%). Bismuth nitrate converts it into mainly mesoxalic acid.

Bromine water, sodium hypobromite or Fenton's reagent ($H_2O_2+FeSO_4$) oxidise it to *glycerose*—a mixture of glyceraldehyde and dihydroxyacetone.

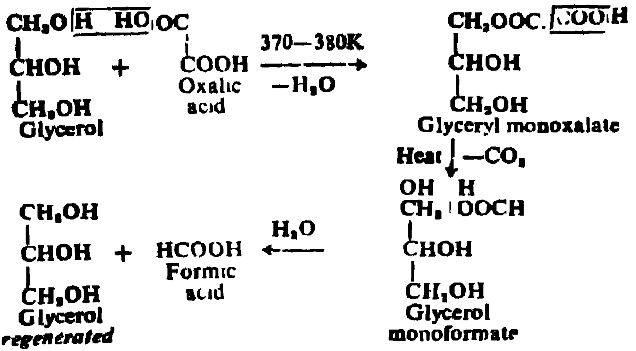
Strong oxidising agents like warm acidified potassium permanganate break it down to oxalic acid, carbon dioxide, etc.

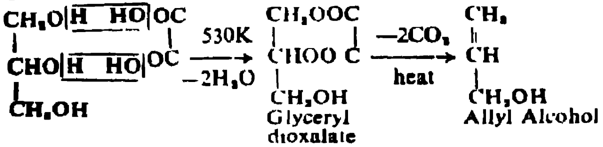
(*vi*) ***Dehydration***. When heated alone or with dehydrating agents like potassium hydrogen sulphate, concentrated sulphuric acid or phosphorus pentoxide, glycerol is dehydrated to form acrolein (acrylaldehyde).



Glycerol

(*vii*) ***Action of Oxalic acid***. When heated with oxalic acid glycerol gives formic acid at 380K while allyl alcohol is produced at 450K.

(a)


(b)


10. Uses.—(*i*) In the manufacture of nitroglycerine, an important explosive.

(*ii*) In the preparation of a number of organic compounds *e.g.*, formic acid, allyl alcohol, etc.

(*iii*) As a softening and moistening agent for tobacco, shaving soaps, shoe polishes, printing inks, type-writer ribbons, leather goods etc.

(*iv*) As a sweetening agent in confectionery and beverages.

(*v*) In the manufacture of cosmetics and transparent soaps.

(*vi*) As an antifreeze in automobile radiators.

(*vii*) In medicine, externally, for soothing inflammation and internally in the form of glycerophosphates (a tonic).

(*viii*) In water-colour pigments, copying inks, stamp pads.

(*ix*) As a lubricant for watches and clocks.

11. Tests for glycerol and distinction from other sugar solutions.—(*i*) It is a colourless, viscous liquid, sweet in taste.

(*ii*) It does not reduce Fehling's solution or ammoniacal silver nitrate (*cf. sugars which are reducing agents*).

(*iii*) When heated with potassium hydrogen sulphate, glycerol gives acrolein which when dissolved in water, gives Schiff's reaction and reduces Fehling's solution and ammoniacal silver nitrate (*see aldehydes*).

(*iv*) On adding a few drops of phenolphthalein to some 1 per cent solution of borax, pink colour is obtained which disappears on adding glycerol. The colour reappears on warming and again disappears on cooling (*distinction from sugars*).

(*v*) When treated with concentrated sulphuric acid, there is no effect in cold and slight yellow colour is obtained on warming (*cf. sucrose which is charred in cold and glucose which is charred on warming*).

(*vi*) With caustic soda there is no change of colour (*cf. glucose which gives yellow colour on warming*).

12. **Structure of Glycerol.**—(1) The molecular formula of glycerol as deduced from its analytical data and molecular weight determination is $C_3H_8O_3$.

(2) The following chemical reactions indicate the presence of three hydroxyl groups in glycerol :

(*i*) With PCl_5 it gives glyceryl trichloride wherein three hydrogen atoms along with three oxygen atoms are replaced by three monovalent chlorine atoms.

$$C_3H_8O_3 \xrightarrow{PCl_5} C_3H_5Cl_3$$

(*ii*) With fuming nitric acid and concentrated sulphuric acid mixture, glyceryl trinitrate is obtained. Here again three hydrogen atoms along with three oxygen atoms are replaced by three nitrate radicals (*monovalent*).

$$C_3H_8O_3 \xrightarrow{HNO_3+H_2SO_4} C_3H_5(NO_3)_3$$

(*iii*) Similarly, with acetic anhydride glycerol forms glyceryl triacetate.

$$C_3H_8O_3 \quad \overset{\text{Acetic anhydride}}{\qquad\qquad} \quad C_3H_5(OOCCH_3)_3$$

All of these reactions indicate that it is a trihydric alcohol. The three hydroxyl groups must be attached to three different carbon atoms. This gives the structural formula of glycerol as :

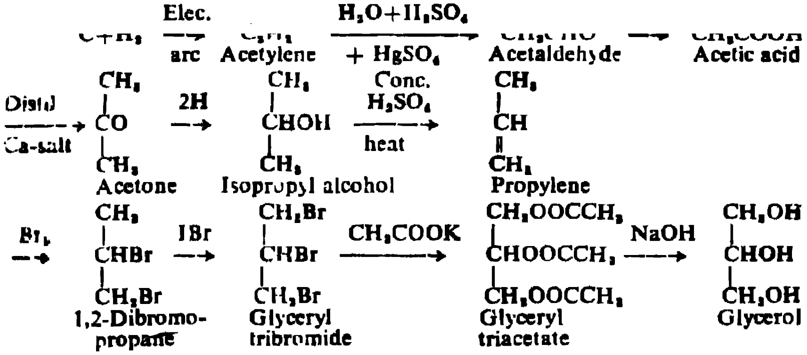
$$CH_2OH—CHOH—CH_2OH.$$

(3) This formula is supported by various products which glycerol gives on oxidation (*see* page 2·161).

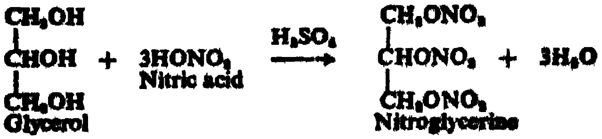
(4) This is confirmed by its synthesis, *e.g.*,

(*i*) From propylene (*see* page 2·159).

(*ii*) From elements, as given below :



13. **Nitroglycerine.**—Nitroglycerine is manufactured by adding glycerol (1 part) in a thin stream to a cold mixture of concentrated sulphuric acid (5 parts) and fuming nitric acid (3 parts). Temperature is not allowed to rise above 300K.



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \\ \text{Glycerol} \end{array} + \begin{array}{l} 3HONO_2 \\ \text{Nitric acid} \end{array} \xrightarrow{H_2SO_4} \begin{array}{l} CH_2ONO_2 \\ | \\ CHONO_2 \\ | \\ CH_2ONO_2 \\ \text{Nitroglycerine} \end{array} + 3H_2O$$

Nitroglycerine separates as a colourless oil and constitutes the upper layer in the reaction mixture. It is removed, washed with ice-cold water and then with dilute solution of sodium carbonate. It is again washed with water and finally dried by filtration through a mat of sponges.

It is glyceryl trinitrate, an ester, not a nitro compound. The incorrect name appears to have been introduced due to the use of nitric and sulphuric acids mixture in the preparation, which is normally used for nitration.

Nitroglycerine is a colourless oily liquid, insoluble in water and poisonous in nature. Usually it burns quietly when ignited but explodes violently when heated rapidly, struck or detonated. It is believed that during explosion, nitroglycerine decomposes as follows, and the gases formed occupy 10,900 times the volume of nitroglycerine.

$$4C_3H_5(ONO_2)_3 \rightarrow 12CO_2+10H_2O+6N_2+O_2$$

It is used in the manufacture of explosives given below and as a stimulant for the heart.

Dynamite. Alfred Nobel (1867), a Swedish chemist and engineer, found that nitroglycerine could be stabilized by absorbing it in kieselguhr. This was *Dynamite*. It is, however, now usually prepared by absorbing nitroglycerine in saw-dust and adding solid ammonium nitrate.

Blasting gelatine or gelignite. It is obtained by making nitroglycerine with gun-cotton (*cellulose nitrate*).

Cordite. It is a mixture of nitroglycerine, gun-cotton and vaseline and is used as smokeless powder.

14. Estimation of the Number of Hydroxyl Groups in a Polyhydric Alcohol.—A known weight (say, W g) of the acetyl derivative of the polyhydric alcohol is refluxed with a known volume of a standard alkali (*excess*). The unused alkali left over is titrated back with standard acid solution and thus the amount of the alkali actually used for hydrolysis of the acetyl derivative is found out. Let it be w g.

$$\begin{array}{llll} X(OH)_n \longrightarrow & X(O.COCH_3)_n & \xrightarrow{nKOH} & X(OH)_n+nCH_3COOK \\ \text{Polyhydric} & \text{Acetyl deriv.} & \text{or} & \\ \text{alcohol} & \text{(Mol. wt.} & 56n \text{ g} & \\ \text{(Mol. wt.}=M) & =M-n+43n & \text{KOH} & \\ & =M+42n) & & \end{array}$$

As is clear from the equation, $M+42n$ g of acetyl derivative require $56n$ g of KOH.

Actually W g of the acetyl derivative require w g of KOH, whence $M+42n$ g of the acetyl derivative will require

$$=\frac{w}{W}(M+42n) \text{ g of KOH.}$$

Equating this with $56n$, we get

$$\frac{w}{W}(M+42n)=56n$$

whence n can be calculated.

Example. *0·218 g of the acetyl derivative of a polyhydric alcohol (mol. wt.=92) requires 0·168 g KOH for hydrolysis. Calculate the number of hydroxyl groups in the alcohol.*

Here $W=0\cdot218$ g ; $w=0\cdot168$ g ; $M=92$.

Substituting these values in the equation

$$\frac{w}{W}(M+42n)=56n, \text{ we get}$$

$$\frac{0\cdot168}{0\cdot218}(92+42n)=56n$$

or $$(92+42n)=\frac{0\cdot218}{0\cdot168}\times56n=\frac{218}{3}n$$

or $$276+126n=218n$$

or $$218n-126n=276$$

or $$92n=276$$

whence $$n=\frac{276}{92}=3$$

i.e., the alcohol is **trihydric.**

QUESTIONS

A. **Essay Type :**

1. What are glycols ? How is ethylene glycol prepared and what are its important properties and uses ? Discuss fully how its constitution is established.

2. How is ethylene oxide prepared ? What are its chief chemical properties ?

3. Describe one method for the manufacture of glycerol. How does it react with—

(*i*) $KHSO_4$, (*ii*) Acetic anhydride,

(*iii*) Oxalic acid at 530K, (*iv*) PI_3 in excess,

(*v*) Cold concentrated sulphuric acid and fuming nitric acid mixture ?

(*Delhi B.Sc. 1976 Supp.* ; *B.Sc. Hons. 1977*)

4. (*a*) Write equations indicating reaction conditions for the formation of the following compounds from glycerol :

(*i*) Propenal, (*ii*) Allyl alcohol,

(*iii*) Glyceryl trinitrate, (*iv*) Glycerol trichlorohydrin.

(*b*) Starting from acetylene, outline the various steps in synthesis of glycerol. (*Delhi B.Sc. Hons 1977*)

5. Discuss the constitution of glycerol. (*Delhi B.Sc. Hons. 1978*)

6. How will you proceed to find whether the given liquid is glycerol ?

7. (*a*) Give the preparation, properties and uses of nitroglycerine ? Why is it so called ?

(*b*) Write a short note on Dynamite.

8. (*a*) Describe the synthesis of glycerol.

(*b*) What is the action of (*i*) HI and (*ii*) oxalic acid on glycerol ?

(*Delhi B.Sc. Hons. Sub. 1978*)

9. How is glycerol manufactured from fats and oils ? What is the action of the following on glycerol (*i*) PCl_5, (*ii*) Na, (*iii*) HCl, (*iv*) $KHSO_4$?

(*Delhi B.Sc. Hons. Sub. 1981*)

B. **Short Answer Type :**

1. How will you convert—

(*i*) Propylene into glycerol, (*ii*) Glycerol into allyl alcohol ?

(*Delhi B.Sc. 1976, 77*)

2. What is Markownikoff's rule ? Would it be applicable to the reactions of ethylene ; of 1-butene ; of 2-butene ; of 2, 3-dimethyl-2-butene ?

(*Delhi B.Sc. 1976* ; *Madras 1976*)

3. Give the reagents and conditions employed for each step involved to bring about the following conversions :

(*i*) Acrolein from glycerol, (*ii*) Glycerol from propene.

(*Delhi B.Sc. 1976, 77*)

4. What happens when glycol is heated with conc. H_2SO_4 ?

(*Delhi B.Sc. Hons 1977*)

5. Give the synthesis of glycerol from ethylene. (*Delhi B.Sc. 1977*)

6. Write structural formulae for

(*a*) 1,5-Pentanediol. (*b*) 2-Methyl-2,4-pentanediol
(*c*) Propylene glycol. (*d*) Pentamethylene glycol
(*e*) $\alpha:\omega$-Dihydroxyheptane. (*f*) 1,2,3-Propanetriol.
(*g*) 2 : 4-Epoxyhexane.

7. What is an antifreeze ?

8. Why is glycol suitable for use as an antifreeze ?

9. Boiling point of glycol (=400K) is much higher than that of 1-propanol (=370·2K) and 2-propanol (=355·6K) even though all the three compounds have roughly the same molecular weight. How can you account for this fact ?

10. Specific gravity increases from methanol (=0·792) to glycol (=1·113) and further to glycerol (=1·261). How can you account for the progressive increase in specific gravity ?

C. **Problems :**

1. An organic compound on analysis was found to contain C=39·13 and H=8·64 with a vapour density of 46. It gave the following reactions :

(*a*) On oxidation with nitric acid it gave a dibasic acid.

(*b*) With P_4O_{10}, it gave an unsaturated aldehyde.

(*c*) With PCl_5 it gave a chlorinated hydrocarbon with V.D. 73·5. What structural formulae would you assign to the compound ? Explain the above reactions.

2. An organic compound of the formula $C_3H_8O_3$ yields on acetylation with acetic anhydride a derivative of the formula $C_9H_{14}O_6$. How many hydroxy groups are present in the substance ? What possible structure will you assign to it ? Explain with reasons

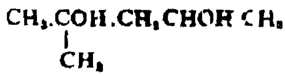
3. A compound of molecular formula $C_5H_{10}O_4$ is changed to $C_{13}H_{18}O_8$ by treatment with acetic anhydride. How many alcohol groups are indicated ?

(*Madurai B.Sc. 1976*)

[**Hint.** $R—OH \xrightarrow{Ac_2O} RO.COCH_3$ For every OH present in alcohol, C_2OH_2 is added. Here total increase is $C_8O_4H_8 \equiv 4OH$].

ANSWERS

B. 6. (*a*) $CH_2OH.CH_2.CH_2.CH_2.CH_2OH$; (*b*)

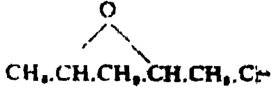


$CH_3.\underset{CH_3}{\underset{|}{C}}OH.CH_2CHOH.CH_3$

(*c*) $CH_3.CHOH.CH_2OH$ (*d*) $CH_2OH.CH_2.CH_2.CH_2.CH_2OH$

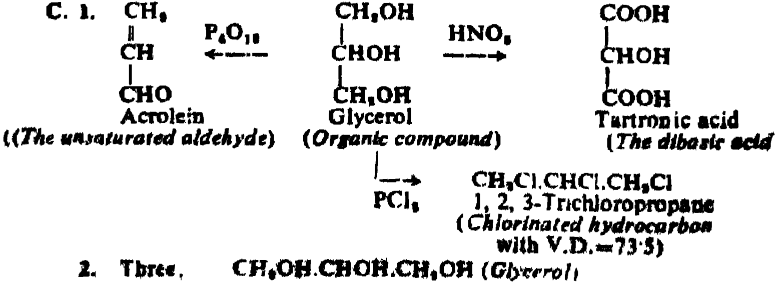
(*e*) $CH_2OH.CH_2.CH_2.CH_2.CH_2.CH_2.CH_2OH$

(*f*) $CH_2OH—CHOH—CH_2OH$ (*g*)



$CH_3.CH.CH_2.CH.CH_2.CH_3$ (O bridging C-2 and C-4)

C. 1.



2. Three, $CH_2OH.CHOH.CH_2OH$ (*Glycerol*)

20

Ethers

1. Ethers are Organic Oxides.—The general formula of the ethers is R—O—R′. These may be directly obtained from alcohol by a process amounting to dehydration.

$$\mathrm{R|\underline{OH + H}|OR' \longrightarrow R.O.R' + H_2O}$$

Alcohol Alcohol Ether
(Alkyl hydroxide) *(Alkyl oxide)*

Derived from aliphatic alcohols or alkyl hydroxides, as they are, ethers may be regarded as the *alkyl oxides* or the *anhydrides of alcohols.*

Just as alcohols may be looked upon as mono-alkyl derivatives of water, ethers may be regarded as di-alkyl derivatives of water, obtained by replacing its both the hydrogen atoms by alkyl groups.

H—O—H	R—O—H	R—O—R
Water	Alcohol *(Mono-alkyl derivative of water)*	Ether *(Dialkyl derivative of water)*

When the two alkyl groups attached to the oxygen atom are the same, the ether is said to be *simple, e.g.,* dimethyl ether $CH_3—O—CH_3$. In case the two alkyl groups are different, the ether is known as *mixed ether, e.g.,* ethyl methyl ether, $CH_3—O—C_2H$

2. Nomenclature.—In the trivial system of nomenclature, the ethers are named according to the alkyl groups attached to the oxygen atom. Simple ethers are given common names, *e.g.*,

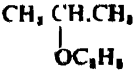
Formula	*Common name*
$CH_3.O\,CH_3$	Dimethyl ether or methyl ether
$C_2H_5\,O.C_2H_5$	Diethyl ether, ethyl ether or simply 'ether'

More complicated ethers are named according to the IUPAC system. According to the IUPAC system of nomenclature, these are regarded as the alkanes in which one hydrogen atom has been replaced by an alkoxy group, —OR. Out of the two alkyl groups, the larger one is chosen as the alkane and the smaller one as alkoxy group. For example,

Formula	*Common name*	*IUPAC name*
$CH_3.O.C_2H_5$	Ethyl methyl ether	Methoxyethane *(mixed ether)*
$C_2H_5.O.C_3H_7$	Ethyl propyl ether	Ethoxypropane *(mixed ether)*

Two isomeric ethoxypropanes are :

$CH_3CH_2CH_2.OC_2H_5$
Ethyl *n*-propyl ether
or 1-Ethoxypropane



$$\mathrm{CH_3\underset{\displaystyle OC_2H_5}{\underset{|}{C}}H.CH_3}$$

Ethyl isopropyl ether
or 2-Ethoxypropane

3. General Methods of Preparation of Ethers.—

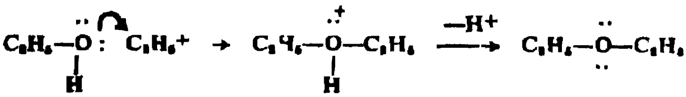
(*i*) *By heating excess of alcohol with concentrated sulphuric acid or glacial phosphoric acid.* One molecule of water is removed from two molecules of alcohol.

$$\underset{\text{Alcohol (Two molecules)}}{\text{RO}\boxed{\text{H} + \text{HO}}\text{R}} \xrightarrow[-\text{H}_2\text{O}]{\text{H}_2\text{SO}_4,\ 410\text{K}} \underset{\text{Ether}}{\text{R}-\text{O}-\text{R}}$$

The mechanism of the reaction is probably :

$$\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{SO}_4 \rightarrow [\text{C}_2\text{H}_5-\text{OH}_2]^+\text{HSO}_4^- \rightarrow \text{C}_2\text{H}_5^+ + \text{H}_2\text{O} + \text{HSO}_4$$

The ethyl-cation, $C_2H_5^+$ may either eliminate a proton and form ethylene (by-product) or react with a molecule of alcohol (present in excess) and form ether as shown below :



$$\text{C}_2\text{H}_5-\underset{\text{H}}{\underset{|}{\ddot{\text{O}}}}: \ \text{C}_2\text{H}_5^+ \rightarrow \text{C}_2\text{H}_5-\underset{\text{H}}{\underset{|}{\overset{+}{\text{O}}}}-\text{C}_2\text{H}_5 \xrightarrow{-\text{H}^+} \text{C}_2\text{H}_5-\ddot{\underset{..}{\text{O}}}-\text{C}_2\text{H}_5$$

The yield is good from primary alcohols and fairly good from secondary alcohols. Tertiary alcohols are readily dehydrated to give olefins and do not give any ether.

(*ii*) *By heating sodium or potassium alkoxide with an alkyl halide* **(Williamson's synthesis)**

$$\underset{\substack{\text{Sodium}\\\text{alkoxide}}}{\text{RO}\boxed{\text{Na} + }} \underset{\substack{\text{Alkyl}\\\text{halide}}}{\boxed{\text{X}}\text{R}'} \longrightarrow \underset{\text{Ether}}{\text{R}-\text{O}-\text{R}'} + \underset{\substack{\text{Sodium}\\\text{halide}}}{\text{NaX}} \qquad (g.)$$

$$\underset{\text{Sodium ethoxide}}{\text{C}_2\text{H}_5\text{ONa}} + \text{BrC}_2\text{H}_5 \longrightarrow \underset{\text{Ethyl ether}}{\text{C}_2\text{H}_5\text{OC}_2\text{H}_5} + \text{NaBr}$$

The mechanism of the reaction is possibly :

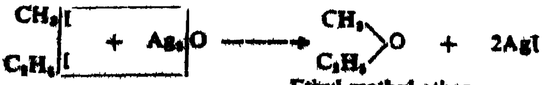
$$\underset{\substack{\text{Alkoxide}\\\text{ion}}}{\text{R}\bar{\text{O}}} \quad \underset{\substack{\text{Alkyl}\\\text{halide}}}{\text{R}'-\text{X}} \rightarrow \underset{\substack{\text{Transition}\\\text{state}}}{\overset{\delta^-}{\text{RO}}\ldots\text{R}'\ldots\overset{\delta^-}{\text{X}}} \rightarrow \underset{\text{Ether}}{\text{R.O.R}'} + \text{X}^-$$

The method is particularly useful for preparing mixed ethers and it is best to use the alkoxide of the secondary and tertiary alcohols and primary alkyl halide. This is desirable because secondary and tertiary alkyl halides decompose readily to give olefins.

(*iii*) *By heating alkyl halide with dry silver oxide.*

$$\underset{\substack{\text{Alkyl}\\\text{halide}}}{2\text{R}\boxed{\text{X}\ +}} \ \underset{\substack{\text{Dry silver}\\\text{oxide}}}{\boxed{\text{Ag}_2}\text{O}} \longrightarrow \underset{\text{Ether}}{\text{R}_2\text{O}} + 2\text{AgX} \qquad (v.g.)$$

Mixed ethers can be prepared by taking two different alkyl halides.



$$\begin{array}{l}\text{CH}_3\text{I}\\\text{C}_2\text{H}_5\text{I}\end{array} + \text{Ag}_2\text{O} \longrightarrow \begin{array}{l}\text{CH}_3\\\text{C}_2\text{H}_5\end{array}\!\!>\text{O} + 2\text{AgI}$$

Ethyl methyl ether

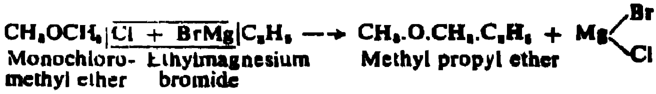
The yield is, however, low as dimethyl ether and diethyl ether are also obtained along with ethyl methyl ether.

(*iv*) *By passing alcohol vapour under pressure over a heated catalyst, e.g., alumina, thoria, etc., at 520K*

$$R\boxed{OH \quad + \quad H}OR \xrightarrow{Al_2O_3} ROR + H_2O$$

In the preparation of ethyl ether from ethanol the yield is about 85%. At about 620K, however, the main product is ethylene (*see* page 2·131).

(*v*) *By the action of Grignard reagent on a lower halogenated ether.*

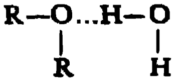


$$\underset{\text{Monochloro-methyl ether}}{CH_2OCH_2}\boxed{Cl + BrMg}\underset{\text{Ethylmagnesium bromide}}{C_2H_5} \longrightarrow \underset{\text{Methyl propyl ether}}{CH_3.O.CH_2.C_2H_5} + Mg\begin{smallmatrix}Br\\Cl\end{smallmatrix}$$

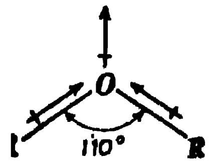
This method is useful for preparing a higher homologue from a lower ether (*Ascent of series*).

4. General Properties of Ethers.—

(*a*) **Physical.** Methyl ether and ethyl methyl ether are gases, other members are colourless, pleasant-smelling, volatile liquids. Their vapours are highly inflammable. They are lighter than water in which they are not very soluble but their solubility is increased by the presence of small amounts of alcohol. The solubility is found to decrease to less than half if water is saturated with common salt. Solubility of ethers is nearly the same as that of their isomeric alcohols. For example, solubility of diethyl ether is nearly the same as that of 1-Butanol (~9 g per 100 g of water). This may possibly be due to hydrogen bonding with molecules of water.



$$\begin{array}{ccc} R-O & \cdots & H-O \\ | & & | \\ R & & H \end{array}$$



Polar ether molecule.

The C—O—C bond angle in ether is about 110° and the molecule is polar. Its dipole moment (=1·18D) is, however, less than that for alcohols. Their boiling points and specific gravities increase gradually with increase in their molecular weights. Lower ethers act as anaesthetics.

(*b*) **Chemical.** As compared with alcohols, ethers are very inert and are not acted upon by alkalis, dilute mineral acids, carboxylic acids, phosphorus pentachloride, metallic sodium, etc. This is due to the fact that there is no active group present in their molecules. Molecular formula of an ether as given below

$$\underset{\text{Alkyl radical}}{R-}\;\underset{\text{Ethereal oxygen}}{-O-}\;\underset{\text{Alkyl radical}}{-R} \quad \text{or} \quad R : \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} : R$$

Electronic formula wherein oxygen atom has two lone pairs of electrons.

consists of two alkyl groups joined through an oxygen atom. Reactions of ether are :

(*i*) **Reactions of the alkyl groups** which resemble alkane.

(*ii*) **Reactions of ethereal oxygen.** Being linked to two carbon atoms, the oxygen atom is comparatively inert. Due to the presence of one pairs of electrons, however, it forms addition compounds with mineral acids (*Oxonium salts*).

(*iii*) **Due to Instability of Carbon to Oxygen linkage.** Unlike carbon to carbon linkage, carbon to oxygen linkage is not very stable. The linkage is ruptured in the presence of a number of reagents giving rise to a variety of products.

Ethers give the following general reactions :

REACTIONS OF THE ALKYL GROUP

(1) **Halogenation.** Ethers give substitution products with chlorine or bromine, the hydrogen atom joined to the carbon atom directly attached to the oxygen atom is most readily replaced. The extent of halogenation depends upon the conditions of the reaction, *e.g.*, in the dark ether reacts with chlorine to give 1,1′-dichloroethyl ether.

$$CH_3CH_2.O.CH_2.CH_3 \xrightarrow{Cl_2} CH_3\,CHCl.O.CH_2.CH_3$$

$$\xrightarrow{Cl_2} CH_3.CHCl.O.CHCl.CH_3$$

In the presence of light, perchlorodiethyl ether is obtained

$$\underset{\text{Ether}}{(C_2H_5)_2O} \xrightarrow{Cl_2} \underset{\text{Perchlorodiethyl ether}}{(C_2Cl_5)_2O}$$

(2) **Burning.** Ethers are highly inflammable and their vapours form explosive mixtures with air (*cf.* alkanes). They burn to produce carbon dioxide and water.

(3) **Peroxide Formation.** Ethers form peroxides in contact with air and light.

$$CH_3CH_2{-}O{-}CH_2CH_3 \xrightarrow[\text{light}]{O_2} CH_3CH(OOH){-}O{-}CH_2CH_3$$

Peroxide is a heavy, pungent, oily liquid and is explosive. Since boiling point of peroxide is higher than that of ether, it is left as residue in the distillation of ether and may cause explosion. Formation of peroxide can be prevented by adding small amount of Cu_2O to ether.

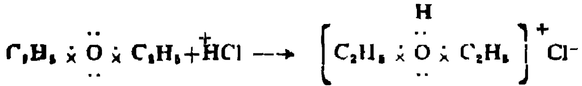
Presence of peroxide in ether can be detected by shaking it with freshly prepared ferrous sulphate solution and then adding potassium thiocyanate solution. Appearance of red colour indicates the presence of peroxide which oxidises Fe^{2+} to Fe^{3+} (gives blood red colour with ^{-}CNS).

Ether can be freed from peroxide by shaking with ferrous salt solution or distilling with conc H_2SO_4.

REACTIONS OF ETHEREAL OXYGEN

(4) **Formation of Oxonium Salts.** Ethers form stable salts (oxonium compounds) with strong inorganic acids. For example, ethyl ether gives $[(C_2H_5)_2OH]^+Cl^-$ and $[C_2H_5)_2OH]^+HSO_4^-$ respectively. Thus ether is removed from ethyl bromide by shaking with concentrated sulphuric acid.

Formation of oxonium salts is analogous to the formation of ammonium salts from ammonia and acids. The two resemble each other in their electronic structure.



$$C_2H_5 \overset{\cdot\cdot}{\underset{\cdot\cdot}{\times O \times}} C_2H_5 + \overset{+}{H}Cl \longrightarrow \left[C_2H_5 \overset{\overset{H}{\cdot\cdot}}{\underset{\cdot\cdot}{\times O \times}} C_2H_5\right]^+ Cl^-$$

Oxonium salt

Oxonium salts are stable only at low temperature and in the presence of concentrated acids. On dilution they dissociate into the original ether and the acid.

REACTIONS DUE TO INSTABILITY OF THE CARBON TO OXYGEN LINKAGE

(5) **Hydrolysis.** When heated with dilute sulphuric acid under pressure, ethers are hydrolysed to the corresponding alcohols.

$$ROR + H_2O \xrightarrow{H_2SO_4} 2ROH$$

$$\underset{\text{Ethyl ether}}{C_2H_5OC_2H_5} + H_2O \xrightarrow{H_2SO_4} \underset{\text{Ethanol}}{2C_2H_5OH}$$

(6) **Action of concentrated Sulphuric acid.** When warmed with concentrated sulphuric acid ethers form alkyl hydrogen sulphates.

$$C_2H_5.O.C_2H_5 + H_2SO_4 \longrightarrow C_2H_5HSO_4 + C_2H_5OH$$

$$C_2H_5OH + H_2SO_4 \longrightarrow C_2H_5HSO_4 + H_2O$$

(7) **Action of Hydriodic acid.** Ethers are readily attacked by concentrated hydriodic acid and final products depend on the temperature of the reaction.

(*i*) *In cold,* it gives an alcohol and alkyl iodide. In the case of mixed ethers, the iodine attaches itself to the smaller alkyl radical.

$$\underset{\text{Ethyl ether}}{C_2H_5|OC_2H_5} + H|I \longrightarrow \underset{\text{Ethyl iodide}}{C_2H_5I} + \underset{\text{Ethanol}}{C_2H_5OH}$$

$$\underset{\text{Ethyl methyl ether}}{CH_3|OC_2H_5} + H|I \longrightarrow \underset{\text{Methyl iodide}}{CH_3I} + \underset{\text{Ethanol}}{C_2H_5OH}$$

This can be explained on the assumption that the reaction proceeds by S_N2 mechanism. The larger group exerts steric effect and the I^-, therefore, attacks the smallar alkyl group (CH_3 here).

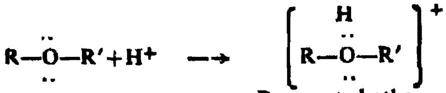
(*ii*) *When heated*, two molecules of alkyl iodide are formed,

$$R—O—R + 2HI \longrightarrow 2RI + H_2O$$

$$C_2H_5—O—C_2H_5 + 2HI \longrightarrow 2C_2H_5I + H_2O$$

With halogen acids in general, the order of reactivity is HI > HBr > HCl

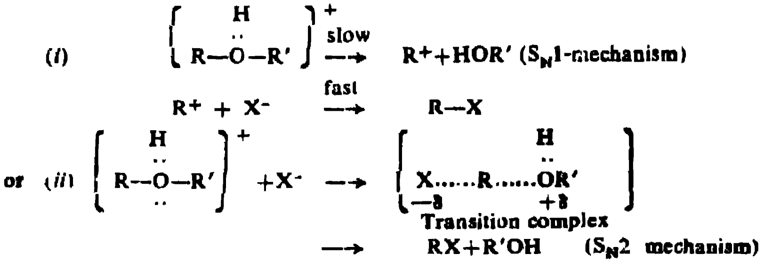
The first reaction is probably formation of protonated ether which then reacts *with halide ion either by S_N1 or S_N2 mechanism. A primary alkyl group* tends to undergo S_N2 *displacement while* S_N1 *displacement is favoured in case* of a tertiary alkyl group.



$$R-\ddot{\underset{\cdot\cdot}{O}}-R'+H^+ \longrightarrow \left[R-\overset{H}{\ddot{\underset{\cdot\cdot}{O}}}-R'\right]^+$$

Protonated ether

Followed by



$$(i)\quad \left[R-\overset{H}{\ddot{O}}-R'\right]^+ \xrightarrow{\text{slow}} R^+ + HOR' \ (S_N1\text{-mechanism})$$

$$R^+ + X^- \xrightarrow{\text{fast}} R-X$$

$$\text{or}\quad (ii)\quad \left[R-\overset{H}{\ddot{\underset{\cdot\cdot}{O}}}-R'\right]^+ + X^- \longrightarrow \left[\underset{-\delta}{X}\ldots\ldots R\ldots\ldots\underset{+\delta}{\overset{H}{\ddot{O}R'}}\right]$$

Transition complex

$$\longrightarrow RX+R'OH \quad (S_N2 \text{ mechanism})$$

(8) **Action of Phosphorus pentachloride.** In the cold, phosphorus pentachloride has no action on ethers but the reaction takes place on heating.

$$R-O-R+PCl_5 \longrightarrow 2RCl + POCl_3$$
$$C_2H_5.O.C_2H_5+PCl_5 \longrightarrow 2C_2H_5Cl + POCl_3$$

(9) **Reaction with Acetyl chloride.** Ethers react when heated with acetyl chloride in the presence of anhydrous zinc chloride as follows :

$$\underset{\text{Ether}}{(C_2H_5)_2O} + \underset{\text{Acetyl chloride}}{CH_3COCl} \xrightarrow[\text{Heat}]{ZnCl_2} \underset{\text{Ethyl chloride}}{C_2H_5Cl} + \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5}$$

5. Spectroscopic Analysis of Ethers.—

Infrared spectra. The C–O group (stretch) in acylic ethers containing two primary alkyl groups, *i.e.*, with structure

$$-CH_2-O-CH_2-$$

gives a characteristic absorption band is the region 1150-1060 cm^{-1}(*s*).

NMR spectra. In the NMR spectra of various methyl ethers ($ROCH_3$) the CH_3O group shows one bond with τ-value of 6-6·7 ppm (δ 3·3-4).

INDIVIDUAL MEMBERS

5. **Dimethyl Ether, Methyl Ether, $(CH_3)_2O$.**—Methyl ether can be prepared by using any of the general methods of preparation. It is manufactured by passing methanol vapours at 620-670K and compressed at 15 atmospheres pressure over aluminium phosphate (*catalyst*).

It is a gas (b.p. 247·6K) very soluble in water. It gives all the reactions characteristic of ethers in general. It is used as a refrigerating agent and low temperature solvent.

6. Diethyl Ether, Ethyl Ether (*Ether,* Sulphuric ether*) **$(C_2H_5)_2O$.**—Ethyl ether is the most important member of ether series and is often referred to simply as *ether.*

It is prepared in the laboratory and industrially by the **Williamson's continuous etherification process,** *i.e., by heating ethanol (in excess) with concentrated sulphuric acid.*

$$\underset{\text{Ethanol (Two molecules)}}{C_2H_5O|\overline{\underline{H + HO}}|C_2H_5} \xrightarrow[-H_2O]{H_2SO_4\ 410K} \underset{\text{Ether}}{C_2H_5.O.C_2H_5}$$

The catalytic action of sulphuric acid is explained as follows .

$$C_2H_5OH+H_2SO_4 \longrightarrow C_2H_5HSO_4 + H_2O$$

$$\underset{\text{Ethyl hydrogen sulphate}}{C_2H_5|\overline{\underline{HSO_4}}} + \underset{\text{Ethanol (excess)}}{\overline{\underline{H}}|O\,C_2H_5} \longrightarrow \underset{\text{Ether}}{C_2H_5O.C_2H_5} + \underset{\text{Sulphuric acid (regenerated)}}{H_2SO_4}$$

Expt. A mixture of ethanol (2 vol.) and concentrated sulphuric acid (1 vol.) is taken in a distillation flask fitted with a thermometer and dropping funnel containing alcohol (Fig. 20·1)

The flask is heated on a sand bath and the temperature maintained at 410K. Alcohol is added at the same rate at which ether distils over and is collected in a receiver cooled in ice-cold water. The process is continuous and is, therefore, called the *continuous etherification process.*

Purification. Ether obtained is contaminated with water, alcohol and sulphurous acid. It is washed with caustic soda solution to remove sulphurous acid and then agitated with 50% solution of calcium chloride to remove alcohol It is next washed with water, dried over anhydrous calcium chloride and redistilled.

In commerce, conc. sulphuric acid is taken in a big pot fitted with steam coils. Alcohol is then added and the mixture is heated by passing steam through the steam coils. The temperature is maintained at 410K (~140°C) and more alcohol is slowly run into the pot.

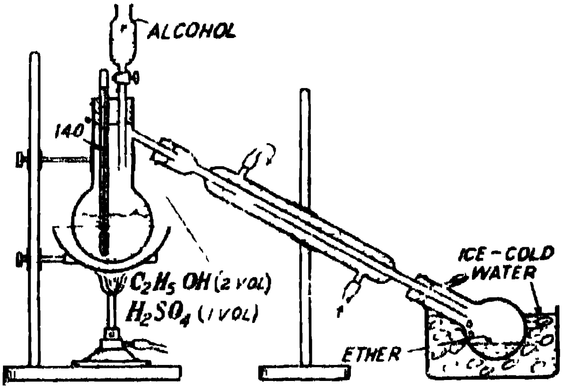


Fig. 20·1—Laboratory preparation of ether.

Vapours of ether and some alcohol mixed with steam and acid fumes escape through the exit provided near the top of the pot. These vapours are washed with dilute alkali solution in the scrubber to remove acid fumes. The vapours are next passed through a fractionating column wherein alcohol and steam condense. The condensate is sent to alcohol recovery tower. Vapours of ether are next condensed by passing through a condenser. Thus alcohol being continuously added to the pot, ether is continuously distilling over.

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* Formerly ethyl ether was supposed to contain sulphur and was, therefore, named *sulphuric ether.* The name is retained even today by some manufacturers probably on account of the use of sulphuric acid in its preparation.

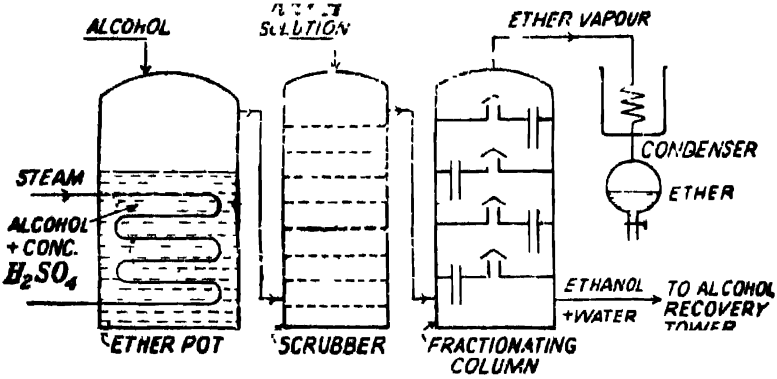


Fig. 20 2—Flow-sheet for the manufacture of ether.

Some other methods used for the manufacture of ether are :

(i) *As a by-product in the manufacture of ethanol from* ***ethylene*** *and sulphuric acid* (*see* page 2 137). Ether is formed as a result of the side reaction.

$$2C_2H_4 + H_2SO_4 \rightarrow \underset{\text{Ethyl sulphate}}{(C_2H_5)_2SO_4}$$

$$(C_2H_5)_2SO_4 + \underset{\substack{\text{Ethanol}\\ \text{formed as a result}\\ \text{of the main reaction}}}{C_2H_5OH} \rightarrow \underset{\text{Ether}}{(C_2H_5)_2O} + C_2H_5HSO_4$$

(ii) *By passing ethanol vapours under pressure over* ***heated alumina*** *or aluminium phosphate as catalyst.*

$$\underset{\text{Ethanol (Two molecules)}}{C_2H_5O\,\underline{|\overline{H} \qquad \overline{HO}|}\,C_2H_5} \xrightarrow[-H_2O]{\text{Heated } Al_2O_3} \underset{\text{Ether}}{C_2H_5OC_2H_5}$$

7. **Properties of Ether.—Physical.** It is a colourless, mobile, highly volatile liquid (b.p. 307·5K) with a pleasant and burning taste. It is only slightly soluble in water, is more soluble in organic solvents and is a solvent itself. It is lighter than water (Sp. Gr. 0·72) and vapours produce unconsciousness.

Chemical. Like all other ethers, it is very inert chemically and is not acted upon by metallic sodium, alkalis, cold phosphorus pentachloride, dilute acid and potassium permanganate, etc. (*cf.* ethanol). It is highly inflammable and its vapours form an explosive mixture with air.

$$C_2H_5OC_2H_5 + 6O_2 \longrightarrow 4CO_2 + 5H_2O$$

Its important reactions have already been discussed under general reactions of ether.

8. **Uses.**—*Ether finds use : (i) As a solvent for* **carrying out Grignard reactions and as an industrial solvent for oils, gums, resins, etc. Also as an extracting solvent.**

(*ii*) As anaesthetic in surgery.

(*iii*) As refrigerant.

9. Structure of Ether.—(*i*) The molecular formula of ether as deduced from its analytical data and molecular weight determination is $C_4H_{10}O$

(*ii*) Ether reacts neither with sodium nor with phosphorus pentachloride in the cold. This shows that *there is no hydroxyl group present in the molecule.*

(*iii*) With hydriodic acid in the cold, ether gives ethyl iodide and ethyl alcohol. *This indicates the presence of two ethyl groups joined through an oxygen atom* as given below

$$C_2H_5{-}O{-}C_2H_5$$

(*iv*) This is further confirmed by the following synthesis of ether :

$$\underset{\text{Sodium ethoxide}}{C_2H_5O\,Na} + \underset{\text{Ethyl iodide}}{I\,C_2H_5} \longrightarrow \underset{\text{Ether}}{C_2H_5{-}O{-}C_2H_5} + NaI$$

10. Isopropyl Ether, $(CH_3)_2CH\,O\,CH(CH_3)_2$.—Isopropyl ether is manufactured by passing propylene into 75% sulphuric acid at 348-398K under 3-7 atmospheres pressure when a molecule of water is added to two molecules of propylene

$$2CH_3CH{=}CH_2 + H_2O \longrightarrow (CH_3)_2CH\,O\,CH(CH_3)_2$$

It is a colourless liquid (b.p. 345K) with a pear-like odour. It finds use as an industrial solvent for decreasing knocking of petrol.

11. β β′-Dichloroethyl Ether, $(CH_2Cl\,CH_2)_2O$.—It is manufactured by dehydrating ethylene chlorohydrin with conc. sulphuric acid at 370K

$$2CH_2Cl\,CH_2OH \xrightarrow{H_2SO_4} (CH_2Cl\,CH_2)_2O + H_2O$$

It is an excellent solvent and is used under the name chlorex for dissolving impurities from lubricating oils.

12. Vinyl Ether, $(CH_2{=}CH)_2O$.—This typical unsaturated ether is obtained by the action of alkali on 2, 2′-dichloroethyl ether

$$(CH_2ClCH_2)_2O + 2KOH \xrightarrow{\text{Heat}} (CH_2{=}CH)_2O + 2KCl + H_2O$$

It is a highly inflammable liquid (b.p. 301.3K). Chemically it resembles both ethylene and ether and is an anaesthetic better than ether.

13. How are Ethers distinguished from Alcohols ?—The following tests may be employed to distinguish ethers from alcohols

Test	Alcohols	Ethers
1. Odour	Sweet alcoholic	Pleasant ethereal
2. Solubility	Miscible with water	Immiscible
3. Action of sodium	Hydrogen liberated, sodium alkoxide (RONa) formed	No action
4. Action of phosphorus pentachloride	Alkyl chloride is formed	No action in cold, alkyl chloride obtained in hot only.
5. Action with CH_3COCl	*Ester formed.*	*React when heated in the* presence of anhydrous $ZnCl_2$ to give RCl + Ester
6. Oxidation.	Easy, Primary alcohols give aldehydes, and Secondary alcohols give ketones. Tertiary alcohols are not easily oxidised.	Possible only with strong oxidising agents, e.g., H_2CrO_4

14. Estimation of the number of methoxy groups in a compound (Zeisel's method).—The reaction between an ether and hydriodic acid is used in the estimation of methoxy or ethoxy groups in a compound. A known weight (say, *w* g) of the compound of mol. wt.=M is treated with 57% hydriodic acid when methoxy or ethoxy groups change into the corresponding iodide.

$$R{-}OCH_3+HI \longrightarrow R{-}OH+CH_3I$$

The methyl or ethyl iodide thus liberated is absorbed in alcoholic silver nitrate solution when silver iodide is precipitated. The precipitate is filtered, washed, dried and weighed (=*W* g say)

$$CH_3I+AgNO_3+H_2O \longrightarrow CH_3OH+AgI+HNO_3$$

One mole of silver iodide precipitate corresponds to the presence of one methoxy or one ethoxy group as the case may be. In the above case weight of silver iodide obtained from one mole =M g of compound containing methoxy groups

$$=\frac{W}{w}\times M \text{ g} \quad \text{or} \quad \frac{WM}{w\times 235}=x \text{ mole of AgI.}$$

Hence number of methoxy groups present in the molecule=*x*

QUESTIONS

Essay Type :

1. (*a*) Describe the preparation of diethyl ether in the laboratory.

(*b*) Explain the action of the following reagents on diethyl ether :

(*i*) hot HI, (*ii*) Cl_2, (*iii*) PCl_5, (*iv*) dil H_2SO_4 under pressure.
(*Delhi B Sc. 1976*)

2. Describe general methods for the preparation of aliphatic ethers.

What reactions do they undergo with (*a*) dilute mineral acid, (*b*) hydriodic acid, (*c*) phosphorus pentachloride ?

3. How may diethyl ether be prepared ? What are its properties and uses ? How would you establish the constitution of an ether ?

4. How would you prepare a pure specimen of diethyl ether. What is its action on (*a*) sodium, (*b*) hydriodic acid, (*c*) phosphorus pentachloride in the cold and hot ? Discuss its structure.

5. What do you understand by cleavage of ethers ? Explain giving examples and write mechanism of the reaction involved.

B. Short Answer Type :

1. What are the difficulties encountered in the preparation of di-*tert*. Butyl ether by the Williamson's method ? (*Delhi B.Sc. Hons. 1976*)

2. How will you convert *tert* butyl alcohol into di-*tert* butyl ether ? (*Delhi B Sc. Hons. 1976 ; Madras B.Sc. 1978*)

3. What test would you perform to distinguish between : *n*-butyl alcohol and diethyl ether ? (*Delhi B.Sc. Hons. 1976 ; Hons. Sub. 1978*)

4. How is ethanol converted into diethyl ether by Williamson's process ? Write the structures of other ethers isomeric with it.

(*Delhi B Sc. Hons. Sub. 1976*)

5. Name various ethers represented by the molecular formula $C_5H_{12}O$ and write their structural formulae.

6. State how you can distinguish by chemical means between Diethyl ether and methyl propyl ether. (*Agra B.Sc. 1970*)

7. Account for the following :

(*a*) Presence of acid is necessary for the cleavage of ethers.

(*b*) Sometimes explosion occurs during distillation of an ether sample.

8. How is peroxide in ether detected and removed ?

9. C_2H_5Br is freed from traces of ether by shaking with conc. H_2SO_4. Explain why ?

10. How will you distinguish between an alcohol and an ether ?
(*Delhi B.Sc. 1978 Supp.*)

11. Give reasons for the following :

(*i*) Alcohols have higher boiling points than the corresponding isomeric ethers.

(*ii*) Isobutylene is more reactive than ethylene towards HCl.

(*iii*) Diethyl ether behaves as a base. (*Delhi B.Sc. Hons. Sub. 1978*)

12. Write structural formulae of the isomeric ethers of the molecular formula $C_4H_{10}O$ and name them according to the IUPAC system.
(*Madras B.Sc. 1978*)

13. Write giving mechanism what you know about the following : cleavage of ether molecules by acids. (*Punjab B.Sc. 1974, 75, 76*)

14. Discuss, giving mechanism, Williamson's synthesis.
(*Punjabi B.Sc. 1976*)

15. Write a short note on the spectroscopic analysis of ethers.
(*Punjab B.Sc. 1976*)

16. How would you prepare $CH_3—O—CH(CH_3)_2$ starting from methanol and 2-propanol ?

17. 3·11 g of an organic substance B, on Zeisel determination, gave 5·882 g of silver iodide. The molecular weight of B is 124. Calculate the number of methoxy groups in it. (Ag=107·9 ; I=126·9) (*Delhi B.Sc. Hons. 1970*)

18. (*a*) Describe briefly Zeisel method for the estimation of methoxy group.

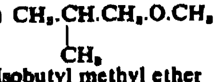
(*b*) In an experiment 4·24 mg of a compound of molecular formula $C_{20}H_{21}O_4N$, when heated with concentrated HI, yields CH_3I which after passing through alcoholic $AgNO_3$ gave 11·62 mg of AgI. Find out the number of methoxy groups in the molecule of the organic compound.
(*Delhi B.Sc. Hons., 1981*)

ANSWERS

Q. 5. (*i*) $CH_3.CH_2CH_2.CH_2O.CH_3$
(*n*-Butyl methyl ether or
1-Methoxybutane)

(*ii*) $CH_3.CH_2.CH_2.O.CH_2CH_3$
(Ethyl *n*-propyl ether or
1-Ethoxypropane)

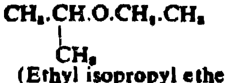
(*iii*)



$CH_3.\underset{\displaystyle CH_3}{\underset{|}{CH}}.CH_2.O.CH_3$

(Isobutyl methyl ether
or 1-Methoxy-2-methylpropane)

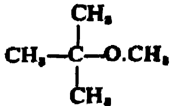
(*iv*)



$CH_3.\underset{\displaystyle CH_3}{\underset{|}{CH}}.O.CH_2.CH_3$

(Ethyl isopropyl ether
(or 2-Ethoxypropane)

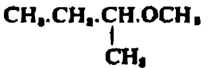
(*v*)



$CH_3—\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}—O.CH_3$

(2-Methoxy-2-methylpropane
or *tert*.-Butyl methyl ether)

(*vi*)



$CH_3.CH_2.\underset{\displaystyle CH_3}{\underset{|}{CH}}.OCH_3$

(2-Methoxybutane
or *sec*.-Butyl methyl ether

16. By reacting CH_3I (from CH_3OH) and $(CH_3)_2)CHONa$ (from 2-propanol).

17. One.

18. Four.

21

Thioalcohols and Thioethers

1. The Aliphatic Sulphur Compounds—Oxygen and sulphur belong to the same group (sub group VIA) of the periodic table and closely resemble each other. The close analogy between them is also manifest in organic compounds containing oxygen. For example,

R—OH	R—O—R	R—CHO	R—CO—R
Alcohol	Ether	Aldehyde	Ketone
R—SH	R—S—R	R—CHS	R—CS—R
Thioalcohol	Thioether	Thio-aldehyde	Thio-ketone

Thioalcohols and thioethers are the most important compounds of these.

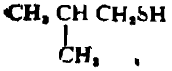
THIOALCOHOLS

2 Thioalcohols, Thiols or Mercaptans, RSH—Being sulphur derivatives of the corresponding alcohols, these are named *thioalcohols or thiols*. These can also be regarded as alkyl derivatives of hydrogen sulphide and are, therefore, named *hydrosulphides*.

$$\underset{\text{Alcohol}}{R{-}O{-}H} \xrightarrow[+S]{-O} \underset{\substack{\text{Thioalcohol or}\\ \text{Alkyl hydrosulphide}}}{R{-}S{-}H} \xleftarrow[+R]{-H} \underset{\substack{\text{Hydrogen}\\ \text{sulphide}}}{H{-}S{-}H}$$

Thioalcohols react with mercuric oxide forming mercuric salts and are, therefore, termed alkyl mercaptans (*mercurium*=mercury ; *captans*=catching). The —SH group is known as *mercapto* or *sulphohydryl* group These compounds occur in petroleum and give rise to 'sour petrol'

3. Nomenclature—Common names for these are alkyl thioalcohols or alkyl mercaptans. Their IUPAC names are obtained by adding the suffix *thiol* to the name of corresponding alkane. For example,

Formula	*Common name*	*IUPAC name*
RSH	Alkyl mercaptan or ,, thioalcohol	Alkanethiol
CH_3SH	Methyl mercaptan or ,, thioalcohol	Methanethiol
C_2H_5SH	Ethyl mercaptan or ,, thioalcohol or simply thioalcohol	Ethanethiol
 $\underset{\displaystyle CH_3}{CH_3\,\underset{\vert}{C}H\,CH_2SH}$	Isobutyl mercaptan or ,, thioalcohol	2-Methyl-propanethiol

The prefix name for the SH group is *mercapto*

$$\overset{\displaystyle SH}{\overset{\vert}{CH_3CHCOOH}}$$

2-mercaptopropanoic acid

4. General Methods of Preparation.—Mercaptans can be prepared :

(*i*) *By heating an alkyl halide with potassium hydrogen sulphide in ethanolic* solution or distilling cheaper potassium alkyl sulphate with potassium hydrogen sulphide.

$$\underset{\text{Ethyl iodide}}{C_2H_5|\boxed{I + K}|SH} \longrightarrow \underset{\text{Ethanethiol}}{C_2H_5SH} + KI \qquad (g)$$

$$\underset{\text{Pot. methyl sulphate}}{CH_3|\boxed{O.SO_2.OK + K}|SH} \longrightarrow \underset{\text{Methanethiol}}{CH_3SH} + K_2SO_4$$

(*ii*) *By heating an alcohol with phosphorus pentasulphide.* The oxygen atom of the alcohol is replaced by sulphur.

$$5C_2H_5OH + P_2S_5 \longrightarrow 5C_2H_5SH + P_2O_5 \qquad (p.)$$

(*iii*) *By passing a mixture of alcohol vapour and hydrogen sulphide over a thoria catalyst at 670K.*

$$ROH + H_2S \xrightarrow{ThO_2} RSH + H_2O \qquad (f.g.)$$

5. Properties.—**Physical.** (*i*) Methanethiol is a gas (b.p. 279K). Ethanol (b.p. 310K) and higher members are colourless volatile liquids with disagreeable smell.

(*ii*) Their boiling points are lower than those of corresponding alcohols. These are also less soluble in water than the corresponding alcohols.

Chemical. Thioalcohols very closely resemble alcohols but the two differ in the following respects :

(*i*) **Acidic character.** Thioalcohols being derivatives of hydrogen sulphide (a weak acid) are weakly acidic in nature and yield metallic derivatives by replacement of acidic hydrogen

$$C_2H_5SH \rightleftharpoons C_2H_5S^- + H^+$$

Alcohols being alkyl derivatives of water (neutral) are neutral in character.

(*ii*) **Oxidation.** In thioalcohols the bivalent sulphur has a tendency to pass to hexavalent state by taking three oxygen atoms and form sulphonic acids.

Chemical reactions of thioalcohols are given below :

(1) **Action of Sodium.** When treated with alkali metals, thiols form mercaptides with the evolution of hydrogen (*cf.* alcohols).

$$\underset{\text{Thioalcohol}}{2C_2H_5SH} + 2Na \longrightarrow \underset{\text{Sod. mercaptide}}{2C_2H_5SNa} + H_2$$

The alkali mercaptides are salts, $[RS]^-Na^+$ and are decomposed by water.

$$C_2H_5SNa + H_2O \rightarrow C_2H_5SH + NaOH$$

The reaction is reversible for lower alkanethiols since they dissolve in aqueous alkali (*Acidic character*).

$$C_2H_5S|\boxed{H + HO}|Na \longrightarrow C_2H_5SNa + H_2O$$

(2) **Formation of Salts.** These react with metallic salts and oxides forming salts (mercaptides).

$$\begin{array}{l} C_2H_5S \\ C_2H_5S \end{array}\boxed{\begin{array}{lr} H & CH_3COO \\ & + \\ H & CH_3COO \end{array}}\Big\rangle Pb \longrightarrow \begin{array}{l} C_2H_5S \\ C_2H_5S \end{array}\Big\rangle Pb + 2CH_3COOH$$

Ethanethiol **Lead mercaptide**

$$\underset{\text{Aqueous suspension}}{2C_2H_5SH} + HgO \longrightarrow \underset{\text{Mercury mercaptide}}{(C_2H_5S)_2Hg} + H_2O$$

(3) **Formation of Thiolesters.** Thiols react with carboxylic acids in the presence of an inorganic acid to form *thiolesters.*

$$CH_3CO\boxed{OH + H}SC_2H_5 \rightleftharpoons \underset{\substack{\text{Ethyl thioacetate}\\ (\textit{Thiolester})}}{CH_3COSC_2H_5} + H_2O$$

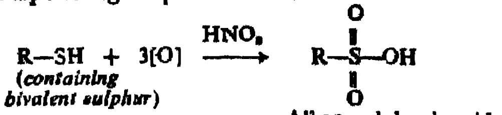
This suggests that esterification involves the hydroxyl of the carboxyl group and hydrogen of the thiol group.

(4) **Oxidation.** Thiols on oxidation give products depending upon the nature of oxidising agents. For example,

(*a*) ***With mild oxidising agents*** like air or hydrogen peroxide, dialkyl disulphides are obtained.

$$2C_2H_5SH + H_2O_2 \longrightarrow \underset{\text{Diethyl disulphide}}{C_2H_5—S—S—C_2H_5} + 2H_2O$$

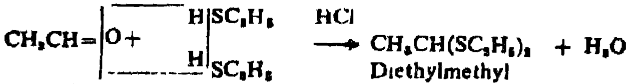
(*b*) ***With strong oxidising agents*** like nitric acid thiols are oxidised to the corresponding sulphonic acids.



$$\underset{\substack{(\textit{containing}\\ \textit{bivalent sulphur})}}{R—SH} + 3[O] \xrightarrow{HNO_3} R—\overset{\overset{\large O}{\|}}{\underset{\underset{\large O}{\|}}{S}}—OH$$

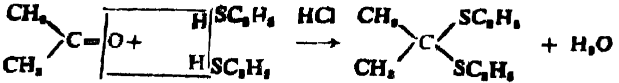
Alkanesulphonic acid
(*containing hexavalent sulphur*)

(5) **Condensation with Aldehydes and Ketones.** Thiols readily condense with aldehydes and ketones in the presence of hydrochloric acid to form *mercaptals* and *mercaptols*, respectively.



$$CH_3CH{=}\boxed{O + \begin{matrix}H\\H\end{matrix}}\begin{matrix}SC_2H_5\\SC_2H_5\end{matrix} \xrightarrow{HCl} CH_3CH(SC_2H_5)_2 + H_2O$$

Acetaldehyde Diethylmethyl mercaptal



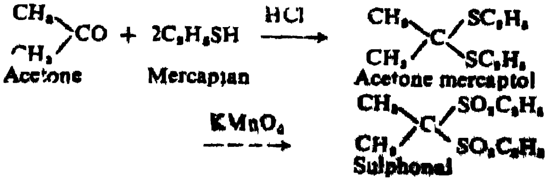
Acetone Diethyldimethyl mercaptol

6. **Uses of Mercaptans.**—(*i*) Ethyl mercaptan is added to natural gas for detecting leakage in gas pipes.

(*ii*) These are used in preparing hypnotics like sulphonal.

(*iii*) These are intermediates in the synthesis of vat dyes.

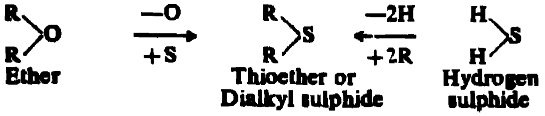
7. **Sulphonal, $(CH_3)_2.C(SO_2C_2H_5)_2$.**—It is prepared by condensing acetone with ethyl mercaptan in the presence of HCl gas and oxidising the acetone mercaptol so obtained with potassium permanganate.



Properties and Uses. Sulphonal is a colourless crystalline solid (m.p. 400K), soluble in hot water. It is used as a sleep-producing drug (*soporific*).

THIOETHERS

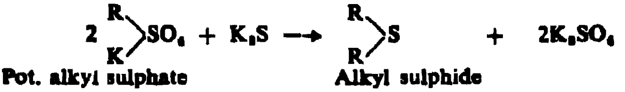
8. Thioethers or Alkyl sulphide.—Thioethers are sulphur analogues of ethers and can also be regarded as dialkyl derivatives of hydrogen sulphide.



9. General Methods of Preparation.—Thioethers are prepared :

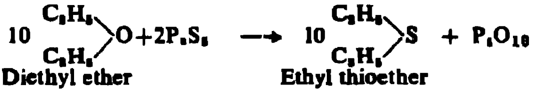
(*i*) *By heating potassium sulphide with an alkyl halide or potassium alkyl sulphate.*

$$2C_2H_5I + K_2S \longrightarrow \underset{\text{Thioether}}{(C_2H_5)_2S} + 2KI \qquad (f.g.\text{-}g.)$$



(*g.*)

(*ii*) *By heating an ether with phosphorus pentasulphide.*



(*g.*)

(*iii*) *By heating an alkyl halide with sodium mercaptide* (*cf.* Williamson's synthesis for preparation of ether—page 2·168)

$$C_2H_5|\overline{I + Na}|\underset{\text{Sod. mercaptide}}{SC_2H_5} \longrightarrow \underset{\text{Thioether}}{(C_2H_5)_2S} + NaI \qquad (g.\text{-}v.g.)$$

(*iv*) *By passing vapours of mercaptan over heated catalyst* (Al_2O_3+ZnS) *at 570K.*

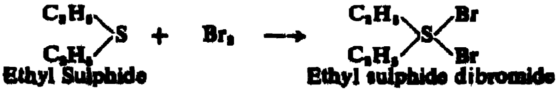
$$\underset{\text{Mercaptan}}{2RSH} \xrightarrow[570K]{Al_2O_3+ZnS} \underset{\text{Thioether}}{R-S-R} + H_2S$$

10. Properties of Thioethers.—

Physical. Thioethers are colourless, neutral, volatile, oily liquids with unpleasant smell. These are insoluble in water but soluble in organic solvents. Their boiling points are higher than the boiling points of corresponding ethers.

Chemical. Chemically thioethers are comparatively inert. Various reactions given by them are :

(*i*) **Addition of Halogens.** Thioethers form addition products with halogens, *e.g.*, with bromine alkyl sulphide dibromide, R_2SBr_2 is formed.



(*ii*) **Addition of Alkyl halides.** Thioethers combine with a molecule of alkyl halide to give *sulphonium salts*. Sulphur is ter-covalent and uni-electrovalent in these salts.

$$\underset{\text{Ethyl thioether}}{(C_2H_5)_2S} + C_2H_5I \longrightarrow \underset{\text{Triethylsulphonium iodide}}{[(C_2H_5)_3\overset{+}{S}:]I^-}$$

On heating the sulphonium salt decomposes into alkyl sulphide and alkyl halide.

$$[(C_2H_5)_3\overset{+}{S}]I^- \longrightarrow (C_2H_5)_2S + C_2H_5I$$

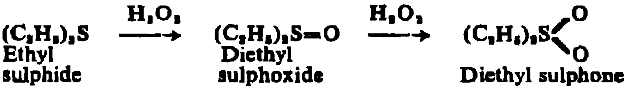
When treated with moist silver oxide, the sulphonium salts yield sulphonium hydroxide.

$$[(C_2H_5)_3\overset{+}{S}]I^- + AgOH \longrightarrow [(C_2H_5)_3\overset{+}{S}]OH^- + AgI$$

Sulphonium hydroxides are strongly basic and decompose on heating to give thioether and olefin, *e.g.*,

$$\underset{\substack{\text{Triethylsulphonium}\\ \text{hydroxide}}}{[(C_2H_5)_3\overset{+}{S}]OH^-} \longrightarrow (C_2H_5)_2S + C_2H_4 + H_2O$$

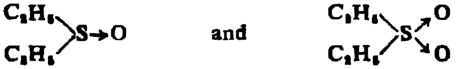
(*iii*) **Oxidation Reactions.** With oxidising agents like hydrogen peroxide in glacial acetic acid, potassium permanganate, nitric acid or chlorine water, thioethers first give sulphoxides and then sulphones.



$$\underset{\substack{\text{Ethyl}\\ \text{sulphide}}}{(C_2H_5)_2S} \xrightarrow{H_2O_2} \underset{\substack{\text{Diethyl}\\ \text{sulphoxide}}}{(C_2H_5)_2S{=}O} \xrightarrow{H_2O_2} \underset{\text{Diethyl sulphone}}{(C_2H_5)_2S\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix}}$$

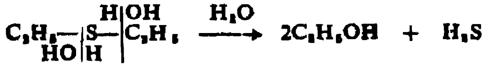
Originally, sulphur was considered to be tetravalent in sulphoxides and hexavalent in sulphones.

Later on, valencies of sulphur were changed to 3 and 4 respectively to satisfy the *octet theory* and formulae of these compounds were written with coordinate bonds as given below :



There is more evidence at present in favour of the previous view and sulphur is believed to be tetravalent and hexavalent.

(*iv*) **Hydrolysis.** On boiling with alkali solution, thioethers are hydrolysed to give the parent alcohol.

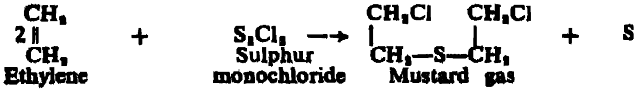


$$C_2H_5{-}S{-}C_2H_5 \xrightarrow{H_2O} 2C_2H_5OH + H_2S$$

Here thioethers behave as esters of hydrogen sulphide.

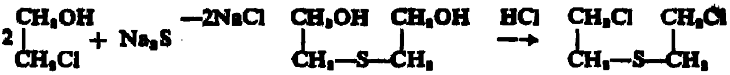
11. Mustard gas, 2 : 2′-Dichlorodiethyl sulphide, $(ClCH_2.CH_2)_2S$.—

Preparation. Mustard gas may be prepared by the action of sulphur monochloride on ethylene.



$$2\underset{\text{Ethylene}}{\begin{matrix}CH_2\\ \|\\ CH_2\end{matrix}} + \underset{\substack{\text{Sulphur}\\ \text{monochloride}}}{S_2Cl_2} \longrightarrow \underset{\text{Mustard gas}}{\begin{matrix}CH_2Cl & & CH_2Cl\\ | & & |\\ CH_2 & -S- & CH_2\end{matrix}} + S$$

In a pure state it may be prepared by heating ethylene chlorohydrin with sodium sulphide and treating the product with hydrochloric acid.



$$2\,\begin{matrix}CH_2OH\\|\\CH_2Cl\end{matrix} + Na_2S \xrightarrow{-2NaCl} \begin{matrix}CH_2OH & & CH_2OH\\|&&|\\CH_2—&S&—CH_2\end{matrix} \xrightarrow{HCl} \begin{matrix}CH_2Cl & & CH_2Cl\\|&&|\\CH_2—&S&—CH_2\end{matrix}$$

Properties and Uses. Mustard gas is an oily liquid (b.p. 488-490K) with a mustard like smell (hence the name). Its vapours are highly vesicant producing painful blisters on the skin. These can penetrate rubber and even thick boots.

The vapours are adsorbed by active charcoal. These are oxidised to sulphoxide (harmless) by chlorine or bleaching powder.

It was used as a poison gas in World War I (1914-18).

QUESTIONS

Essay Type :

1. What are mercaptans ? How do they react with—

(*i*) an aldehyde, (*ii*) an acid chloride,
(*iii*) lead acetate, (*iv*) hydrogen peroxide ?
(*Delhi B.Sc. 1976*)

2. How are mercaptans prepared ? Give their physical and chemical properties. In what respects do they resemble and differ from alcohols ?
(*Jabalpur B.Sc. 1964 ; Punjab 1971*)

3. Describe the preparation and reactions of ethyl mercaptan.

4. How are thioalcohols and thioethers prepared ? Illustrate the statement that chemical behaviour of these compounds is due to the tendency of divalent sulphur to pass to the tetravalent state.

5. How would you prepare sulphonal and what are its chief chemical properties ?

6. What are mercaptans ? Give one method for their preparation. Indicate a method for converting mercaptan into sulphonal.
(*Madras B Sc. 1978*)

Short Answer Type :

1. Write equations for the reactions, between :

(1) Ethyl iodide +(*i*) potassium hydrogen sulphide ; (*ii*) potassium sulphide ; (*iii*) sodium mercaptide ; (*iv*) ethyl thioether.

(2) Potassium methyl sulphate + (*i*) potassium hydrogen sulphide ; (*ii*) potassium sulphide.

(3) Phosphorus pentasulphide + (*i*) ethanol ; (*ii*) ether.

(4) Alcohol+hydrogen sulphide passed over heated thoria.

(5) Mercaptan + (*i*) sodium ; (*ii*) sodium hydroxide ; (*iii*) lead acetate ; (*iv*) mercuric oxide ; (*v*) acetic acid ; (*vi*) hydrogen peroxide ; (*vii*) nitric acid ; (*viii*) acetaldehyde ; (*ix*) acetone and oxidation of the product obtained ; (*x*) passed over heated catalyst (Al_2O_3+ZnS).

(6) Ethyl sulphide+ (*i*) ethanol ; (*ii*) H_2O_2 ; (*iii*) alkali.

(7) Triethylsuphonium iodide+(*i*) heated ; (*ii*) treated with moist silver oxide and the product is heated.

(8) Ethylene+sulphur monochloride.

(9) Ethylene chlorohydrin+Na_2S followed by treatment with HCl.

2. Write the structural formulae for the following compounds :

(*i*) 2-Methyl propanethiol. (*ii*) *iso*-Propyl thioether.
(*iii*) 1-Butanesulphonic acid. (*iv*) *tert*-Butyl sulphide.
(*v*) Diethyl sulphoxide. (*vi*) Dimethyl sulphone.
(*vii*) Mustard gas. (*viii*) Sulphonal.

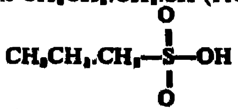
3. How will you proceed to synthesise mustard gas ? Discuss its use as a poisonous gas. (*Punjab B.Sc. 1971*)

4. *n*-Propyl bromide reacts with KSH to yield C_3H_8S (A) which gives with conc. nitric acid $C_3H_8O_3S$ (B). The compound B reacts with PCl_5 and gives a chloride (C). Identify the compounds A, B and C.

ANSWERS

4. A is $CH_3CH_2.CH_2.SH$ (Propanethiol) ;

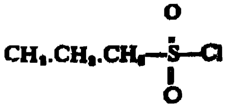
B is



$$CH_3CH_2.CH_2—\overset{\overset{\Large O}{\|}}{\underset{\underset{\Large O}{\|}}{S}}—OH$$

1-Propanesuphonic acid

and C is



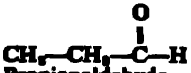
$$CH_3.CH_2.CH_2—\overset{\overset{\Large O}{\|}}{\underset{\underset{\Large O}{\|}}{S}}—Cl$$

1-Propanesulphonyl chloride

22

Aldehydes and Ketones

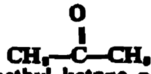
1. Carbonyl Compounds.—Aldehydes and ketones are hydrocarbon derivatives which contain the carbonyl group, $C{=}O$. The compound is an *aldehyde* if the oxygen atom is attached to a *primary* carbon and it is *ketone*, if the oxygen atom is attached to a *secondary* carbon, *e.g.*,



$$CH_3{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H$$

Propionaldehyde
(An aldehyde)

and



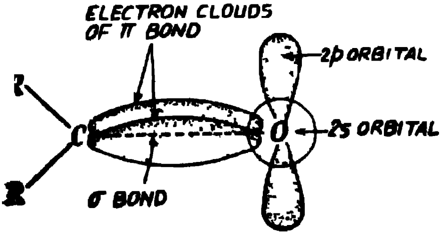
$$CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3$$

Dimethyl ketone or acetone
(A ketone)

(Isomers represented by the molecular formula C_3H_6O)

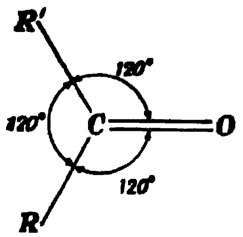
Both aldehydes and ketones have the general formula $C_nH_{2n}O$. The characteristic group of aldehydes is $-CHO$ or $-CH{=}O$ and occurs only at the end of the chain. The characteristic group of ketones is $>C{=}O$ which cannot occur at the end of the chain as each of the two free valencies is joined to a carbon atom. The carbonyl group ($>C{=}O$) is referred to as the ketonic group when it occurs in ketones.

Electronic structure of carbonyl group. In the carbonyl group carbon atom is in a state of sp^2 hybridisation. C—O sigma bond is produced by overlap of an sp^2 orbital of carbon with a p orbital of oxygen. The π bond of the $>C{=}O$ group is formed by the sideway overlap of p orbitals of carbon and oxygen atoms. This leaves two sp^2 hybrid orbitals on carbon atom available for bond formation, and an s and a p orbital on oxygen containing the two lone pairs.

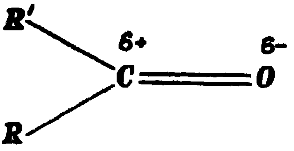


The electronic structure of the carbonyl group

Carbonyl carbon atom is joined to three atoms by σ-bonds. Since these bonds utilize sp^2 orbitals, they lie in the same plane and are 120° apart.

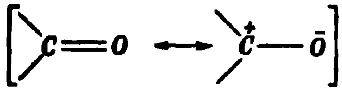


Structure of carbonyl group.



Polarity of carbonyl group.

The carbonyl bond is a double bond composed of a σ-bond and a π-bond. It is polarised. Dipole moments of aldehydes and ketones have shown that the values are larger than can be accounted for by the inductive effect of oxygen atom. This can be accounted for if carbonyl compounds are resonance hybrids.



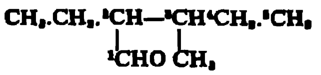
RESONANCE FORMS

Thus the carbon atom has a positive charge and can be attacked by nucleophilic reagents. The carbonyl group also exhibits basic properties ; it is readily protonated by strong acids. Oxygen being more electronegative than carbon the second resonating structure makes a larger contribution than the first.

2. **Nomenclature : Aldehydes.**—The general formula of the aldehydes is RCHO. Their common names are derived from the acids that they form on oxidation. The suffix *-ic acid* is replaced by *-aldehyde*. In the IUPAC nomenclature the name of an aldehyde is derived from the corresponding alkane by replacing the final *e* by *al* as given below ;

Formula	*Corresponding acid*	*Common name*	*IUPAC nam*
HCHO	$\xrightarrow{O}$ HCOOH Formic acid	Formaldehyde	Methanal
$CH_3.CHO$	$\xrightarrow{O}$ CH_3COOH Acetic acid	Acetaldehyde	Ethanal
C_2H_5CHO	$\xrightarrow{O}$ C_2H_5COOH Propionic acid	Propionaldehyde	Propanal
C_3H_7CHO	$\xrightarrow{O}$ C_3H_7COOH Butyric acid	Butyraldehyde	Butanal
$(CH_3)_2CH.CHO$	$\xrightarrow{O}$ $(CH_3)_2CH.COOH$ *iso*-Butyric acid	Isobutyr-aldehyde	2-Methylpropanal

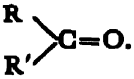
To name higher members, longest chain containing the aldehyde group is selected as the parent hydrocarbon. Numbering is begun with the aldehyde group as number 1 which may be omitted if the aldehydic group is the only functional group present in the compound. For example,



$$CH_3.CH_2.\overset{2}{C}H(\overset{1}{C}HO)—\overset{3}{C}H(CH_3)\overset{4}{C}H_2.\overset{5}{C}H_3$$

is 2-ethyl-3-methylpentanal.

Ketones. The general formula of ketones is



When the two alkyl groups are the same, the ketone is termed to be simple while another with two different alkyl groups is termed a mixed ketone.

The lower members are commonly named according to the alkyl groups attached to the ketonic group. These are also named after the acid from which they are prepared. For example, the ketone obtained by dry distillation of *calcium acetate* is named *acetone*. In the IUPAC system, ketones are designated by the suffix *-one* which is added to the name of the hydrocarbon from which they are derived. A few particular members are :

Formula of the Ketone	*Common name*	*IUPAC name*
$CH_3.CO.CH_3$	Dimethyl ketone or Acetone	Propanone (*Simple*)
$CH_3.CH_2CO.CH_2.CH_3$	Diethyl ketone (*Simple*)	3-Pentanone
$CH_3.CO.CH_2.CH_2.CH_3$	Methyl propyl ketone	2-Pentanone (*Mixed*)

In the case of substituted ketones the positions of side-chains are indicated by Greek letters, α, β, etc. (Trivial system) or numbers (IUPAC system). Carbon atom adjacent to the ketonic group is termed α and the one next to this β. For example,

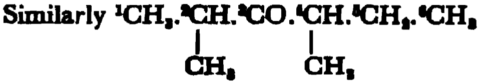
$$\overset{\beta}{C}H_3.\overset{\alpha}{C}HCl.CO.\overset{\alpha'}{C}H_2.\overset{\beta'}{C}H_2Cl$$

is α : β′-dichlorodiethyl ketone (*Trivial name*) or

$$^{5}CH_3.^{4}CHCl.^{3}CO.^{2}CH_2.^{1}CH_2Cl$$

1, 4-dichloro-3-pentanone (*IUPAC name*).

Similarly



$$^{1}CH_3.^{2}\underset{\large CH_3}{\underset{|}{C}H}.^{3}CO.^{4}\underset{\large CH_3}{\underset{|}{C}H}.^{5}CH_2.^{6}CH_3$$

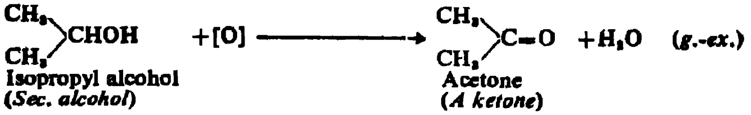
is 2, 4-dimethyl-3-hexanone.

3. General Methods of Preparation of Aldehydes and Ketones.—

(1) *By the oxidation of alcohols with acid dichromate.* Primary alcohols give *aldehydes* whereas secondary alcohols give *ketones.*

$$CH_3CH_2OH + [O] \xrightarrow{\text{Acid dichromate}} CH_3CHO + H_2O \quad (f.g.\text{-}g)$$

Ethanol (*A primary alcohol*) → Acetaldehyde (*An aldehyde*)



$$\begin{matrix}CH_3\\CH_3\end{matrix}\Big\rangle CHOH + [O] \longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\Big\rangle C{=}O + H_2O \quad (g.\text{-}ex.)$$

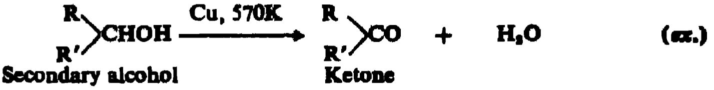
Isopropyl alcohol (*Sec. alcohol*) → Acetone (*A ketone*)

Oxidation may also be effected by passing the alcohol vapours mixed with air over silver catalyst heated to 520K. The yield is about 60-75%.

During preparation of aldehydes by oxidation of primary alcohols, aldehyde must be removed from the reaction mixture as soon as it is formed, otherwise the aldehyde formed will be further oxidised to the corresponding acid.

(2) *By the catalytic dehydrogenation of alcohols.* The vapours of alcohol are passed over heated copper at 570K.

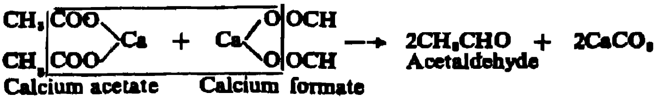
$$\underset{\text{Primary alcohol}}{R.CH_2OH} \xrightarrow{Cu,\ 570K} \underset{\text{Aldehyde}}{R.CHO} + H_2 \qquad (ox.)$$



$$\underset{\text{Secondary alcohol}}{\begin{matrix}R\\R'\end{matrix}\!\!>CHOH} \xrightarrow{Cu,\ 570K} \underset{\text{Ketone}}{\begin{matrix}R\\R'\end{matrix}\!\!>CO} + H_2O \qquad (ox.)$$

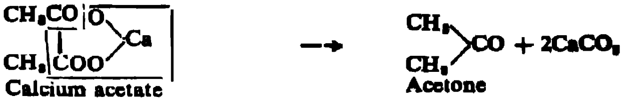
In this process there is no risk of further oxidation of aldehyde obtained.

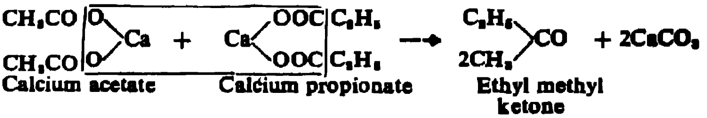
(3) *By heating calcium salts of fatty acids.* An aldehyde is obtained when calcium salt is heated with calcium formate. A ketone is obtained when calcium salts other than formate are heated.



The yield is poor as a ketone (acetone here) and formaldehydes are also obtained along with the aldehyde (acetaldehyde here).

$$\underset{\text{Cal. formate}}{(HCOO)_2Ca} \longrightarrow \underset{\text{Formaldehyde}}{HCHO} + CaCO_3$$





Yield is poor for mixed ketones, because in addition to mixed ketone (ethyl methyl ketone here) simple ketones (acetone and diethyl ketone here) are also obtained.

Barium, manganese and thorium salts give better yield of ketone than the calcium salts.

(4) *By passing the vapours of fatty acids over manganese oxide as catalyst at 570K.* An aldehyde is obtained if formic acid is one of the two acids otherwise a ketone is formed.

$$\underset{\text{Acetic acid}}{CH_3|\overline{COOH}} + \underset{\text{Formic acid}}{\overline{HO}|OCH} \xrightarrow{MnO} \underset{\text{Acetaldehyde}}{CH_3CHO} + CO_2 + H_2O \qquad (f.g.\text{-}g.)$$

$$\underset{\text{(Acetic acid \textit{two molecules})}}{CH_3CO/\overline{OH} + \overline{HOOC}|CH_3} \xrightarrow{MnO} \underset{\text{Acetone}}{CH_3COCH_3} + CO_2 + H_2O \qquad (g.)$$

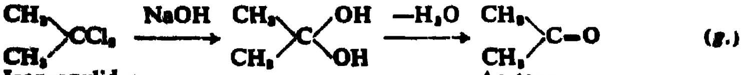
Probably manganous salts are obtained as intermediate products which decompose to give an aldehyde or a ketone and manganous carbonate. The latter decomposes at 570K to regenerate the catalyst.

$$MnCO_3 \longrightarrow MnO + CO_2$$

A mixture of fatty acids gives mixed ketones. The yield is however, low as explained above.

(5) ***By hydrolysis of alkylidene halides.***

$$\underset{\text{Ethylidene chloride}}{CH_3.CHCl_2} \xrightarrow{NaOH} \underset{\text{Dihydric alcohol (unstable)}}{CH_3CH(OH)_2} \xrightarrow{-H_2O} \underset{\text{Acetaldehyde}}{CH_3CHO}$$



Isopropylidene chloride
Acetone

This method is not used much since aldehydes are affected by alkali and the dihalides are usually prepared from the carbonyl compounds.

(6) ***Aldehydes are obtained by the reduction of acid chlorides with hydrogen in boiling xylene in the presence of a catalyst—palladium suspended in barium sulphate*** (**Rosenmund's reaction**).

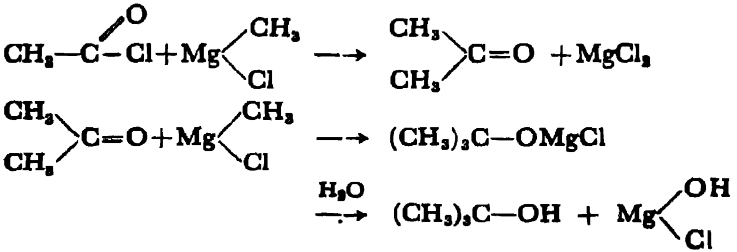
$$\underset{\text{Acetyl chloride}}{CH_3COCl} + H_2 \longrightarrow \underset{\text{Acetaldehyde}}{CH_3CHO} + HCl \qquad (g.\text{-}v.g.)$$

Aldehydes are more readily reduced than the acid chlorides but the final product is not an alcohol. This is because of barium sulphate which acts as a poison for the palladium catalyst and prevents the aldehyde from being reduced to alcohol. Generally a small amount of quinoline and sulphur is added. These are very effective in poisoning the catalyst.

Ketones are prepared by the action of dialkylcadmium on acid chlorides.

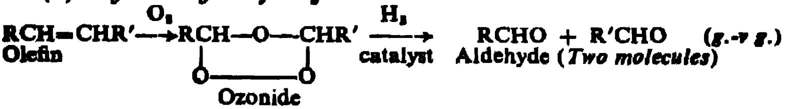
$$2RCOCl + R'_2Cd \longrightarrow 2RCOR' + CdCl_2$$

Grignard reagent also reacts with acid chloride to give a ketone but the ketone obtained reacts further with one more molecule of Grignard reagent to produce a tertiary alcohol.

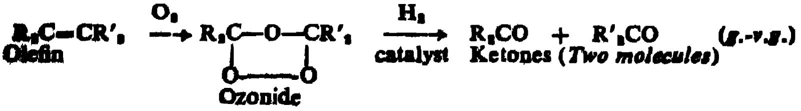


Hence dialkylcadmium is superior to Grignard reagent for the preparation of ketones.

(7) *By ozonolysis of olefins*

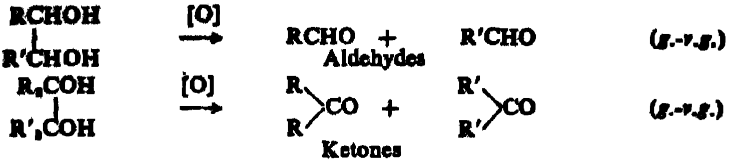


$$\underset{\text{Olefin}}{RCH{=}CHR'} \xrightarrow{O_3} \underset{\text{Ozonide}}{RCH{-}O{-}CHR'}\ (O{-}O) \xrightarrow[\text{catalyst}]{H_2} \underset{\text{Aldehyde (Two molecules)}}{RCHO + R'CHO} \qquad (g.\text{-}v.g.)$$



$$\underset{\text{Olefin}}{R_2C{=}CR'_2} \xrightarrow{O_3} \underset{\text{Ozonide}}{R_2C{-}O{-}CR'_2}\ (O{-}O) \xrightarrow[\text{catalyst}]{H_2} \underset{\text{Ketones (Two molecules)}}{R_2CO + R'_2CO} \qquad (g.\text{-}v.g.)$$

(8) *By the oxidation of 1, 2-glycols with lead tetra-acetate or periodic acid.*



$$\begin{matrix}RCHOH\\ |\\ R'CHOH\end{matrix} \xrightarrow{[O]} \underset{\text{Aldehydes}}{RCHO + R'CHO} \qquad (g.\text{-}v.g.)$$

$$\begin{matrix}R_2COH\\ |\\ R'_2COH\end{matrix} \xrightarrow{[O]} \underset{\text{Ketones}}{\begin{matrix}R\\R\end{matrix}\!\!>\!CO + \begin{matrix}R'\\R'\end{matrix}\!\!>\!CO} \qquad (g.\text{-}v.g.)$$

(9) *By addition of water to acetylene or its derivatives in presence of 42% sulphuric acid containing mercuric sulphate as catalyst.* Acetylene gives acetaldehyde whereas its homologues yield ketones.

$$\underset{\text{Acetylene}}{CH\equiv CH} + H_2O \longrightarrow \underset{\text{Acetaldehyde}}{CH_3CH=O} \qquad (v.g.)$$

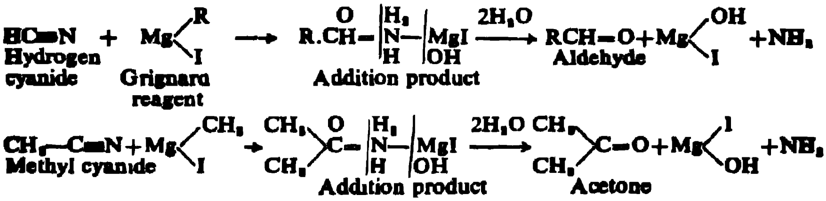
$$\underset{\text{Allylene}}{CH_3.C\equiv CH} + H_2O \longrightarrow \underset{\text{Acetone}}{CH_3CO.CH_3} \qquad (g.)$$

(10) *By reduction of an alkyl cyanide dissolved in ether with stannous chloride and hydrochloric acid and hydrolysis of the imino-chloride so obtained with water* (**Stephen's method**).

$$\overset{H\ \ H}{RC\equiv N} \xrightarrow[+HCl]{SnCl_2} \underset{\text{Iminochloride}}{\overset{O\qquad H_2}{RCH=NH.HCl}} \xrightarrow{H_2O} RCHO + NH_4Cl$$

There is no analogous method for the preparation of ketones.

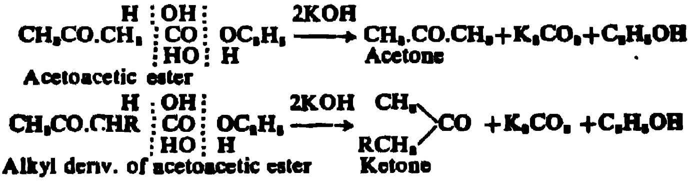
(11) *From Grignard reagent which gives aldehydes with hydrogen cyanide and ketones with alkyl cyanides.*



$$\underset{\text{Hydrogen cyanide}}{HC\equiv N} + \underset{\text{Grignard reagent}}{Mg\begin{matrix}R\\I\end{matrix}} \longrightarrow \underset{\text{Addition product}}{R.\overset{O}{CH}=\begin{vmatrix}H_2\\N\\H\end{vmatrix}\!-\!\begin{vmatrix}\\MgI\\OH\end{vmatrix}} \xrightarrow{2H_2O} \underset{\text{Aldehyde}}{RCH=O} + Mg\begin{matrix}OH\\I\end{matrix} + NH_3$$

$$\underset{\text{Methyl cyanide}}{CH_3-C\equiv N} + Mg\begin{matrix}CH_3\\I\end{matrix} \rightarrow \underset{\text{Addition product}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!\overset{O}{C}=\begin{vmatrix}H_2\\N\\H\end{vmatrix}\!-\!\begin{vmatrix}\\MgI\\OH\end{vmatrix}} \xrightarrow{2H_2O} \underset{\text{Acetone}}{\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C=O} + Mg\begin{matrix}I\\OH\end{matrix} + NH_3$$

(12) *Ketones are prepared by the ketonic hydrolysis of the alkyl derivative of acetoacetic ester by boiling with dilute acid or dilute alkali, preferably acid solution.*



$$\underset{\text{Acetoacetic ester}}{CH_3CO.\overset{H}{CH_2}\ \begin{matrix}OH\\CO\\HO\end{matrix}\ \begin{matrix}\\OC_2H_5\\H\end{matrix}} \xrightarrow{2KOH} \underset{\text{Acetone}}{CH_3.CO.CH_3} + K_2CO_3 + C_2H_5OH$$

$$\underset{\text{Alkyl deriv. of acetoacetic ester}}{CH_3CO.\overset{H}{CHR}\ \begin{matrix}OH\\CO\\HO\end{matrix}\ \begin{matrix}\\OC_2H_5\\H\end{matrix}} \xrightarrow{2KOH} \underset{\text{Ketone}}{\begin{matrix}CH_3\\RCH_2\end{matrix}\!>\!CO} + K_2CO_3 + C_2H_5OH$$

For mechanism of Ketonic hydrolysis see chapter 30, *page 2·341.*

There is no analogous method for the preparation of aldehydes.

4. General Properties of Aldehydes and Ketones.—

(*a*) **Physical**. (*i*) Except formaldehyde which is a gas, lower aldehydes and ketones are colourless volatile liquids. Higher ones are solids.

(*ii*) Lower aldehydes possess rather unpleasant smell while ketones have a pleasant odour. Higher aldehydes have a fruity odour.

(*iii*) Formaldehyde, acetaldehyde and acetone are freely soluble in water. Solubility decreases with the rise in molecular weight and members with five or more carbon atoms are insoluble.

Solubility of lower members in water is due to some hydrogen bonding between >C=O group and water molecule and smaller size of alkyl group. Solubility decreases as the size of alkyl group (hydrocarbon part) increases.

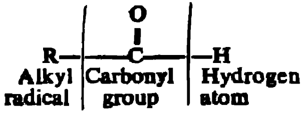
(*iv*) Other physical constants have a regular gradation. Isomeric aldehydes and ketones do not differ widely from each other in their physical constants.

Aldehydes and ketones are polar compounds because of the >C=O group. Intermolecular forces in them are stronger than in hydrocarbon molecules but weaker than those in alcohols having hydrogen bonds. Hence their boiling points lie between hydrocarbons and alcohols of comparable masses. For example

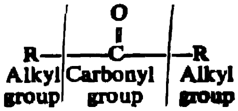
Compound :	*n*-Butane	*n*-Butyraldehyde	*n*-Butyl alcohol
Boiling point (*K*) :	309	349	391

(*v*) Acetone and other lower ketones are very good solvents and are widely used as such.

(*b*) **Chemical.** Both aldehydes and ketones contain the alkyl group and carbonyl group as given below :

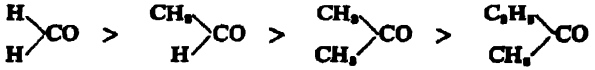


An Aldehyde



A Ketone

This accounts for the large number of reactions common to both aldehydes and ketones. It has been found that the reactivity of carbonyl group depends on the nature of alkyl groups attached to it. Smaller the alkyl group, the more reactive is the carbonyl group. For example, the order of reactivity is as given below :



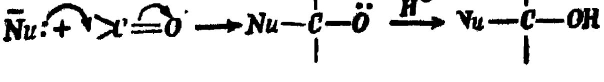
$$\begin{matrix}H\\H\end{matrix}\!\!>CO \;>\; \begin{matrix}CH_3\\H\end{matrix}\!\!>CO \;>\; \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CO \;>\; \begin{matrix}C_2H_5\\CH_3\end{matrix}\!\!>CO$$

The large groups protect the carbon of the carbonyl group from the attacking nucleophile.

The lonely hydrogen in aldehydes is very reactive and is readily oxidised to OH group. This along with the order of reactivity as given above accounts for the reactions in which aldehydes and ketones differ.

Two principal reactivities common to aldehydes and ketones are

(*i*) ***Nucleophilic addition reactions to the carbonyl group.***



$$\bar{N}u: + \;>C=O \longrightarrow Nu-\overset{|}{\underset{|}{C}}-\ddot{\bar{O}} \xrightarrow{H^{\oplus}} Nu-\overset{|}{\underset{|}{C}}-OH$$

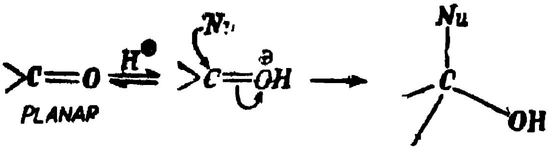
(ii) *Active hydrogen reactions* in which the α-hydrogen is removed by base and the resulting enolate anion serves as a nucleophile for attack on other molecules (*see* page 2·198).

(1) Nucleophilic Addition reactions of the Carbonyl group.

The part of the compounds containing the carbonyl is flat (planar), the π electrons being above and below in a direction perpendicular to the plane of the group, the nucleophilic reagents attack at these places. The typical reaction is that of *nucleophilic addition*. As a result of such addition the carbonyl C (which is sp^2 hybridised) acquires tetrahedral configuration around it (sp^3 hybridised).

The real cause of the reactivity of the carbonyl group towards nucleophiles is the tendency of the oxygen atom to acquire electrons—its ability to carry a negative charge and impart positive charge to carbonyl carbon.

A typical acid catalysed addition of a nucleophile will be as follows :



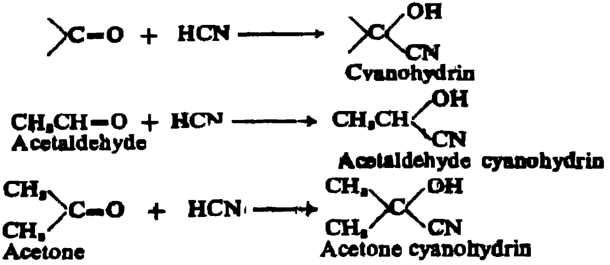
Undergoes nucleophilic attack more readily

Tetrahedral

In the presence of acid, the carbonyl group gets protonated. *This prior protonation lowers the E_{act} for nucleophilic attack, since it permits oxygen to acquire π electrons without having to accept a negative charge.*

The alkyl groups of ketones, being electron-releasing, make carbonyl C less positive and decreases its tendency for accepting the nucleophile. *Aldehydes undergo nucleophilic addition more readily than ketones.*

(i) *Addition of Hydrocyanic Acid.* When treated with sodium cyanide and dilute sulphuric acid the carbonyl group adds on hydrogen cyanide to form **cyanohydrins**.



$$>C{=}O + HCN \longrightarrow >C\begin{matrix}OH\\CN\end{matrix} \qquad (g.\text{-}v.g.)$$

Cyanohydrin

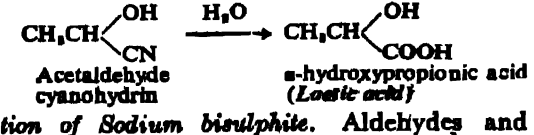
$$CH_3CH{=}O + HCN \longrightarrow CH_3CH\begin{matrix}OH\\CN\end{matrix}$$

Acetaldehyde — Acetaldehyde cyanohydrin

$$\begin{matrix}CH_3\\CH_3\end{matrix}>C{=}O + HCN \longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}>C<\begin{matrix}OH\\CN\end{matrix}$$

Acetone — Acetone cyanohydrin

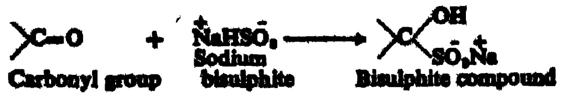
Cyanohydrins are important compounds in organic synthesis as they are readily hydrolysed to α-hydroxy acids.



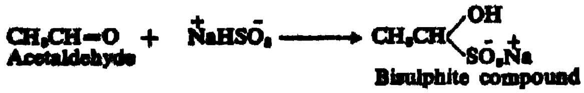
$$CH_3CH\begin{matrix}OH\\CN\end{matrix} \xrightarrow{H_2O} CH_3CH\begin{matrix}OH\\COOH\end{matrix}$$

Acetaldehyde cyanohydrin — α-hydroxypropionic acid (*Lactic acid*)

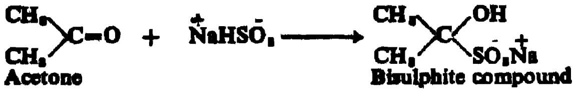
(ii) *Addition of Sodium bisulphite.* Aldehydes and ketones add on sodium bisulphite to give crystalline bisulphite compounds. These on heating with dilute acid or sodium carbonate solution regenerate the original aldehyde or ketone. This reaction affords a convenient method of separating aldehydes and ketones from non-carbonyl compounds.



$$\underset{\text{Carbonyl group}}{>C=O} + \underset{\substack{\text{Sodium}\\ \text{bisulphite}}}{\overset{+}{Na}HS\overset{-}{O}_3} \longrightarrow \underset{\text{Bisulphite compound}}{>C<^{OH}_{S\overset{-}{O}_3\overset{+}{Na}}}$$

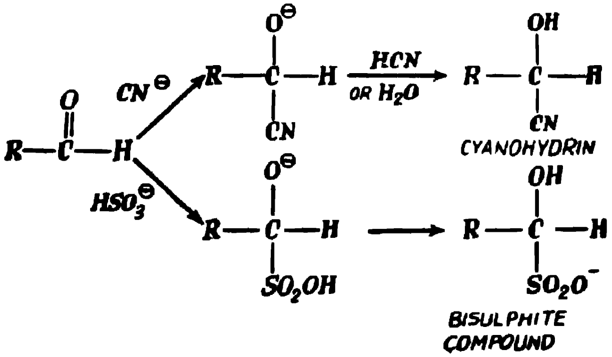


$$\underset{\text{Acetaldehyde}}{CH_3CH=O} + \overset{+}{Na}HS\overset{-}{O}_3 \longrightarrow \underset{\text{Bisulphite compound}}{CH_3CH<^{OH}_{S\overset{-}{O}_3\overset{+}{Na}}}$$



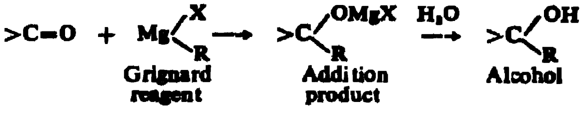
$$\underset{\text{Acetone}}{{}^{CH_3}_{CH_3}>C=O} + \overset{+}{Na}HS\overset{-}{O}_3 \longrightarrow \underset{\text{Bisulphite compound}}{{}^{CH_3}_{CH_3}>C<^{OH}_{S\overset{-}{O}_3\overset{+}{Na}}}$$

Mechanism of the formation of cyanohydrin and bisulphite has been suggested as follows :



The carbonyl group >C=O undergoes electromeric effect at the requirement of the attacking reagent. Positively charged carbon atom is attacked by the *nucleophilic* reagent while negatively charged oxygen atom is attacked by *electrophilic* reagent. Positively charged carbon being less stable arrangement is attacked first and the negatively charged oxygen being more stable arrangement is attacked later.

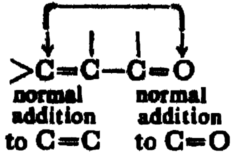
(*iii*) *Addition of Grignard reagent.* The carbonyl group adds on Grignard reagent and the addition product on hydrolysis yields an alcohol. For example, formaldehyde gives primary alcohols, other aldehydes form secondary alcohols while ketones yield tertiary alcohols (*see* page 2'126).



$$>C=O + \underset{\substack{\text{Grignard}\\ \text{reagent}}}{Mg<^{X}_{R}} \longrightarrow \underset{\substack{\text{Addition}\\ \text{product}}}{>C<^{OMgX}_{R}} \xrightarrow{H_2O} \underset{\text{Alcohol}}{>C<^{OH}_{R}}$$

Addition to Conjugated Aldehydes and Ketones. Conjugated dienes may undergo 1, 2- or 1, 4- addition as discussed on page 2'49. In unsaturated aldehydes and ketones when the >C=O group is conjugated with the >C=C<, the resulting *enone* may also undergo these two modes of addition. 1, 2- additions are called *normal additions* whereas 1, 4-additions are often termed *conjugate additions*.

Conjugate addition



$$>C=\overset{|}{C}-\overset{|}{C}=O$$

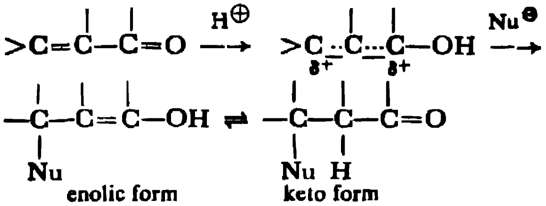
The overall result of **electrophilic addition to enones** appears to be an anti-Markownikoff addition to C=C. Actually, however, it is the result of 1, 4-addition followed by tautomerism.

Mechanism of the Conjugate electrophilic addition. It involves the following steps :

(*i*) Addition of electrophile H^+ to O of C=O group.

(*ii*) Addition of $Nu^\ominus$ to C of C=C when an enol is formed.

(*iii*) Tautomerism to give the keto form.



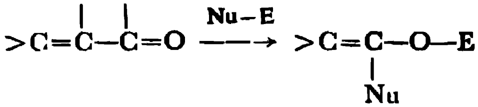
$$>C=\overset{|}{C}-\overset{|}{C}=O \xrightarrow{H^\oplus} >\underset{\delta+}{C}\cdots\overset{|}{C}\cdots\underset{\delta+}{\overset{|}{C}}-OH \xrightarrow{Nu^\ominus}$$

$$-\underset{\underset{Nu}{|}}{\overset{|}{C}}-\overset{|}{C}=\overset{|}{C}-OH \rightleftharpoons -\underset{\underset{Nu}{|}}{\overset{|}{C}}-\underset{\underset{H}{|}}{\overset{|}{C}}-\overset{|}{C}=O$$

1, 2-Addition to C=O group in this case would result in the formation of $>C=\underset{\underset{Nu}{|}}{C}-OH$ which is generally unstable.

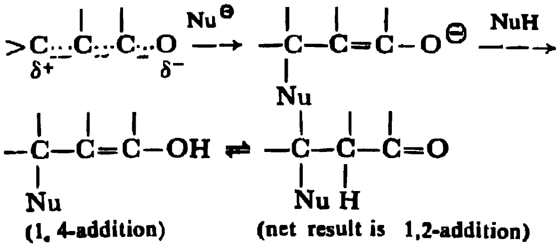
In nucleophilic addition to enones both normal and conjugate addition is possible,

Normal nucleophilic addition :



$$>C=\overset{|}{C}-\overset{|}{C}=O \xrightarrow{Nu-E} >C=\underset{\underset{Nu}{|}}{C}-O-E$$

Conjugate nucleophilic addition :



$$>\underset{\delta+}{C}\cdots\overset{|}{C}\cdots\overset{|}{C}\cdots\underset{\delta-}{O} \xrightarrow{Nu^\ominus} -\underset{\underset{Nu}{|}}{\overset{|}{C}}-\overset{|}{C}=\overset{|}{C}-O^\ominus \xrightarrow{NuH}$$

$$-\underset{\underset{Nu}{|}}{\overset{|}{C}}-\overset{|}{C}=\overset{|}{C}-OH \rightleftharpoons -\underset{\underset{Nu}{|}}{\overset{|}{C}}-\underset{\underset{H}{|}}{\overset{|}{C}}-\overset{|}{C}=O$$

(2) **Addition-Elimination Reactions.** A variety of ammonia derivatives, NH_2—G give acid catalysed nucleophilic addition reactions with >C=O group but the reaction is followed by elimination of H_2O molecule from the addition product.

$$>C{=}O \xrightarrow[H^+]{H_2N{-}G} >C{=}N{-}G + H_2O$$

(*i*) *With Hydroxylamine*—NH_2OH. Aldehydes and ketones, when treated with hydroxylamine, form **oximes** which are known as *aldoximes* and *ketoximes* respectively. They are usually well-defined crystalline solids and may be used to identify aldehydes and ketones.

$$>C{=}\boxed{O + H_2}NOH \longrightarrow >C{=}NOH + H_2O \quad (v.g.)$$

Carbonyl group Hydroxylamine Oxime (*An aldoxime or ketoxime*)

$$CH_3CH{=}\boxed{O + H_2}NOH \longrightarrow CH_3CH{=}NOH + H_2O$$

Acetaldoxime

$$(CH_3)_2C{=}\boxed{O + H_2}NOH \longrightarrow (CH_3)_2C{=}NOH + H_2O$$

Acetone Acetoxime

(*ii*) *With Hydrazine*—$NH_2.NH_2$. Aldehydes and ketones react with hydrazine to give **hydrazones**.

$$>C{=}\boxed{O + H_2}N.NH_2 \longrightarrow >C{=}N.NH_2 + H_2O$$

Hydrazine Hydrazone

$$CH_3CH{=}\boxed{O + H_2}N.NH_2 \longrightarrow CH_3CH{=}N.NH_2 + H_2O$$

Acetaldehyde

$$(CH_3)_2C{=}\boxed{O + H_2}N.NH_2 \longrightarrow (CH_3)_2C{=}N.NH_2 + H_2O$$

Acetone

(*iii*) *With Phenylhydrazine*—$C_6H_5NHNH_2$. Phenylhydrazine reacts with carbonyl group to form **phenylhydrazones**.

$$>C{=}\boxed{O + H_2}N.NHC_6H_5 \longrightarrow >C{=}N.NHC_6H_5 + H_2O$$

Phenylhydrazine Phenylhydrazone

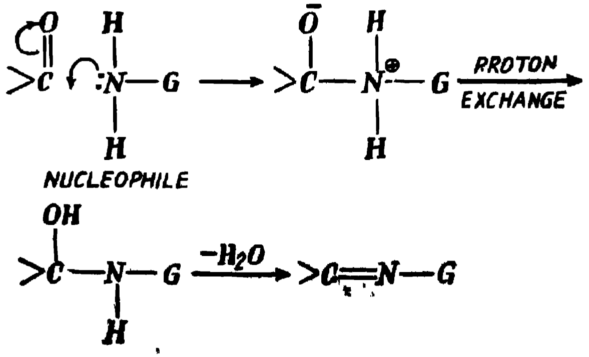
$$CH_3CH{=}\boxed{O + H_2}N.NHC_6H_5 \longrightarrow CH_3CH{=}N.NHC_6H_5 + H_2O$$

Acetaldehyde

$$(CH_3)_2C{=}\boxed{O + H_2}N.NHC_6H_5 \longrightarrow (CH_3)_2C{=}N.NHC_6H_5 + H_2O$$

Acetone

Mechanism of Addition-Elimination Reactions with NH_2OH, $NH_2.NH_2$, $NH_2.NHC_6H_5$, etc. (H_2N—G in general—derivatives of NH_3). The reaction is carried out in *acidic solutions*.



Nucleophilic Addition is followed by proton exchange and elimination of H_2O.

(*iv*) ***With Semicarbazide***—$NH_2.CO.NH.NH_2$. Semicarbazide reacts with the carbonyl group to form well-defined crystalline compounds called **Semicarbazones.**

$$>C=\boxed{O + H_2}N.NHCONH_2 \rightarrow >C=N.NHCONH_2 + H_2O$$

$$CH_3CH=\boxed{O + H_2}N.NHCONH_2 \rightarrow CH_3CH=N.NHCONH_2 + H_2O$$

$$\underset{\text{Acetone}}{(CH_3)_2C=}\boxed{O + H_2}\underset{\text{Semicarbazide}}{N.NHCONH_2} \rightarrow \underset{\text{Semicarbazone}}{(CH_3)_2C=N.NHCONH_2} + H_2O$$

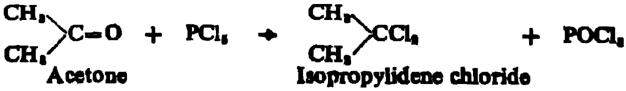
(*v*) ***With thioalcohols*** (*mercaptan*), RSH. Aldehydes and ketones condense with mercaptans to form mercaptals and mercapatol respectively (*see* page 2·180).

$$>C=O + \underset{\text{Mercaptan or thioalcohol}}{2RSH} \rightarrow \underset{\text{Mercaptal or Mercaptol}}{>C(SR)_2} + H_2O$$

(*vi*) ***With Phosphorus pentachloride.*** Phosphorus pentachloride reacts with aldehydes and ketones and replaces the carbonylic oxygen atom by two chlorine atoms.

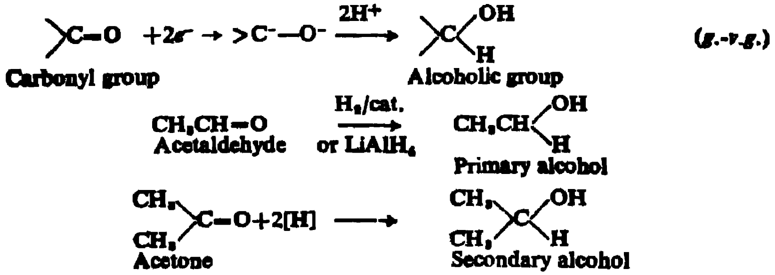
$$>C=O + PCl_5 \rightarrow \underset{\text{Alkylidene chloride}}{>CCl_2} + POCl_3$$

$$\underset{\text{Acetaldehyde}}{CH_3CH=O} + PCl_5 \rightarrow \underset{\text{Ethylidene chloride}}{CH_3CHCl_2} + POCl_3$$



$$\underset{\text{Acetone}}{(CH_3)_2C=O} + PCl_5 \rightarrow \underset{\text{Isopropylidene chloride}}{(CH_3)_2CCl_2} + POCl_3$$

(3) **Reduction.** Aldehydes are reduced catalytically or with dissolving metals to primary alcohols while ketones yield secondary alcohols. The addition takes place in the carbonyl group present in both, as given below. Aldehydes and ketones are, however, conveniently reduced with lithium aluminium hydride, $LiAlH_4$.



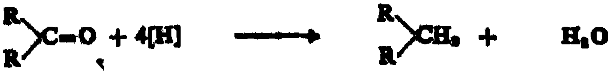
$$\underset{\text{Carbonyl group}}{>C=O} + 2e^- \rightarrow >C^- -O^- \xrightarrow{2H^+} \underset{\text{Alcoholic group}}{>C(OH)H} \quad (g.-v.g.)$$

$$\underset{\text{Acetaldehyde}}{CH_3CH=O} \xrightarrow[\text{or } LiAlH_4]{H_2/cat.} \underset{\text{Primary alcohol}}{CH_3CH(OH)H}$$

$$\underset{\text{Acetone}}{(CH_3)_2C=O} + 2[H] \longrightarrow \underset{\text{Secondary alcohol}}{(CH_3)_2C(OH)H}$$

With concentrated hydriodic acid and red phosphorus the >CO group is reduced to a methylene ($—CH_2—$) group. The same reduction can be effected with amalgamated zinc and concentrated hydrochloric acid (**Clemmensen reduction**).

$$RCH=O + 4[H] \xrightarrow[\text{conc. HCl}]{Zn/Hg} RCH_3 + H_2O$$



$$R_2C=O + 4[H] \longrightarrow R_2CH_2 + H_2O$$

Carbonyl group can also be converted into the methylene group by **Wolff-Kishner reduction**. Hydrazone of the carbonyl compound is heated with C_2H_5ONa at 450K when nitrogen is eliminated resulting in the formation of a methylene group in place of original carbonyl group.

$$\underset{\text{Carbonyl group}}{>C=O} \xrightarrow{NH_2NH_2} \underset{\text{Hydrazone}}{>C=NNH_2} \xrightarrow[450K]{C_2H_5ONa} \underset{\text{Methylene group}}{>CH_2} + N_2$$

Ketones can be reduced to secondary alcohols with aluminium isopropoxide in 2-propanol solution (**Meerwein-Ponndorf reduction**)

$$\underset{\text{Ketone}}{R_2C=O} \xrightarrow[\text{in } Me_2CHOH]{(Me_2CHO)_3Al} \underset{\textit{sec}\text{ alcohol}}{R_2CHOH}$$

(4) **Oxidation.** Aldehydes are easily oxidised to the corresponding acids and on this account, act as strong reducing agents. For example, they reduce ammoniacal solution of silver nitrate (Tollen's reagent) to metallic silver and Fehling's solution (an alkaline solution containing a complex of copper tartrate) to red cuprous oxide.

$$\underset{\text{Acetaldehyde}}{CH_3CH=O} + O \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH}$$

$$RCHO + \underset{\text{Am. silver nitrate soln.}}{2Ag(NH_3)_2^+ + 3OH^-} \longrightarrow RCOO^- + \underset{\text{Silver mirror}}{2Ag} + 4NH_3 + 2H_2O$$

$$RCHO + \underset{\text{From Fehling's solution}}{2Cu^{2+} + 5OH^-} \longrightarrow RCOO^- + 3H_2O + \underset{\substack{\text{Cuprous oxide}\\ (\textit{Red ppt.})}}{Cu_2O}$$

Ketones, on the other hand, are oxidised with difficulty to give acids with less number of carbon atoms. They do not reduce ammoniacal silver nitrate or Fehling's solution.

$$CH_3COCH_3 + 4O \xrightarrow{K_2Cr_2O_7 + H_2SO_4} CH_3COOH + CO_2 + H_2O$$

In the case of mixed ketones, the carbonyl group remains with the smaller alkyl group during oxidation. For example,

$$\underset{\text{Methyl propyl ketone}}{CH_3CO\text{—}CH_2CH_2CH_3} \xrightarrow{[O]} \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Propionic acid}}{CH_3CH_2COOH}$$

(5) **Halogenation.** This is a property of alkyl group in which substitution occurs.

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + 3Cl_2 \longrightarrow \underset{\text{Chloral}}{CCl_3CHO} + 3HCl$$

$$\underset{\text{Acetone}}{CH_3COCH_3} + 3Cl_2 \longrightarrow \underset{\text{Trichloro-acetone}}{CCl_3COCH_3} + 3HCl$$

(6) **Aldol Condensation.** *Union of two or more molecules of the same or different compounds, with or without the elimination of a small molecule such as water, ammonia, methyl alcohol, etc., resulting in the formation of a new substance is called* **Condensation.** Characteristics of the change are :

(*i*) It is an irreversible change.

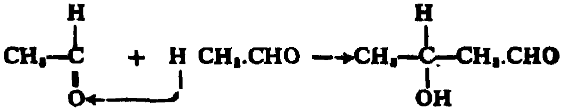
(*ii*) It is a union with or without the elimination of component elements.

(*iii*) New carbon-to-carbon linkage is set up.

(*iv*) Molecular weight of the product may or may not be exact multiple of the molecular weight of the original substance.

For example,

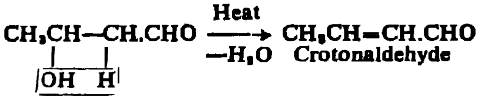
(*a*) In presence of dilute alkali, potassium carbonate or hydrochloric acid two molecules of acetaldehyde condense to give a syrupy liquid known as **aldol.**



$$CH_3-\underset{\underset{O}{\|}}{\overset{\overset{H}{|}}{C}} + H\,CH_2.CHO \longrightarrow CH_3-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-CH_2.CHO$$

Acetaldehyde (*Two molecules*) Aldol

On heating aldols eliminate water to form unsaturated compounds. For example, aldol on heating gives crotonaldehyde.

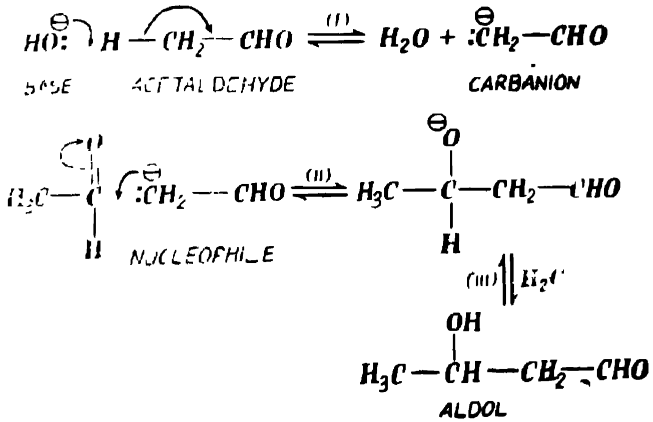


$$CH_3\underset{\underset{OH}{|}}{CH}-\underset{\underset{H}{|}}{CH}.CHO \xrightarrow[-H_2O]{\text{Heat}} CH_3CH{=}CH.CHO$$

Crotonaldehyde

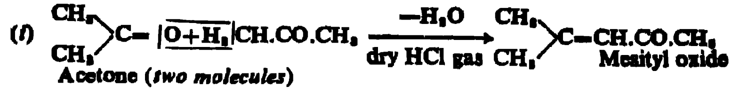
The mechanism of the aldol condensation is probably as given below :

Aldehydes and ketones can add together (aldehyde-aldehyde, or aldehyde-ketone or ketone-ketone) provided an α-hydrogen is available (H at carbon next to carbon of $>C=O$). The mechanism of a *base catalysed* aldol condensation (CH_3CHO and CH_3CHO) is given below :

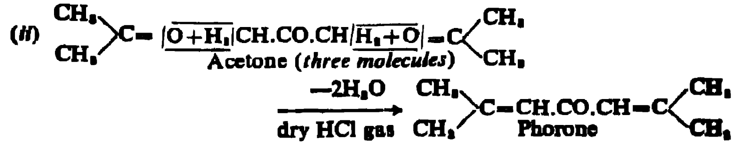


The OH⁻ (catalyst) reacts in step (*I*) to produce the *nucleophile carbanion*. The catalyst is regenerated in the third step.

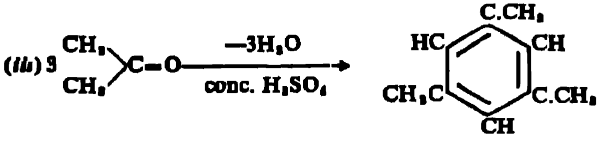
(*b*) In many cases it is the unsaturated compound that is isolated and not the aldol, *e.g.*, condensation products of acetone. In presence of dry hydrogen chloride it gives **mesityl oxide** or **phorone** whereas in presence of concentrated sulphuric acid **mesitylene** is obtained.



$$(i)\quad \underset{\text{Acetone (two molecules)}}{(CH_3)_2C=\boxed{O+H_2}CH.CO.CH_3} \xrightarrow[\text{dry HCl gas}]{-H_2O} \underset{\text{Mesityl oxide}}{(CH_3)_2C=CH.CO.CH_3}$$

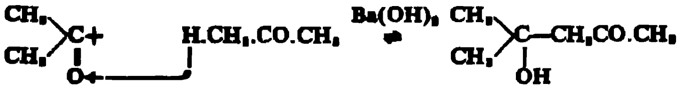


$$(ii)\quad \underset{\text{Acetone (three molecules)}}{(CH_3)_2C=\boxed{O+H_2}CH.CO.CH\boxed{H_2+O}=C(CH_3)_2} \xrightarrow[\text{dry HCl gas}]{-2H_2O} \underset{\text{Phorone}}{(CH_3)_2C=CH.CO.CH=C(CH_3)_2}$$



Mesitylene (*yield*=25%)

(*c*) In the presence of barium hydroxide, acetone gives diacetone alcohol.



$$(CH_3)_2C=O + H.CH_2.CO.CH_3 \overset{Ba(OH)_2}{\rightleftharpoons} \underset{\text{Diacetone alcohol}}{(CH_3)_2C(OH)-CH_2CO.CH_3}$$

The aldol condensation can occur :

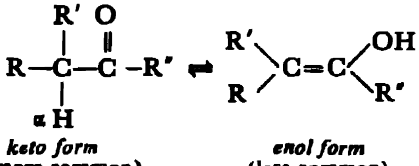
(*i*) between two aldehyde molecules (identical or different) ;

(*ii*) between two ketone molecules (identical or different) ; and

(*iii*) between an aldehyde and a ketone.

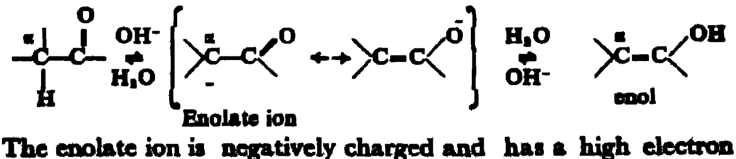
In all cases it is only the α-hydrogen atom which is involved in aldol condensation.

(7) **Enolization.** Aldehydes and ketones possessing an α-hydrogen may undergo tautomerism



$$\underset{\substack{\textit{keto form}\\ \text{(more common)}}}{R-\overset{R'}{\underset{\alpha H}{C}}-\overset{O}{\overset{\|}{C}}-R'} \rightleftharpoons \underset{\substack{\textit{enol form}\\ \text{(less common)}}}{RR'C=C(OH)R'}$$

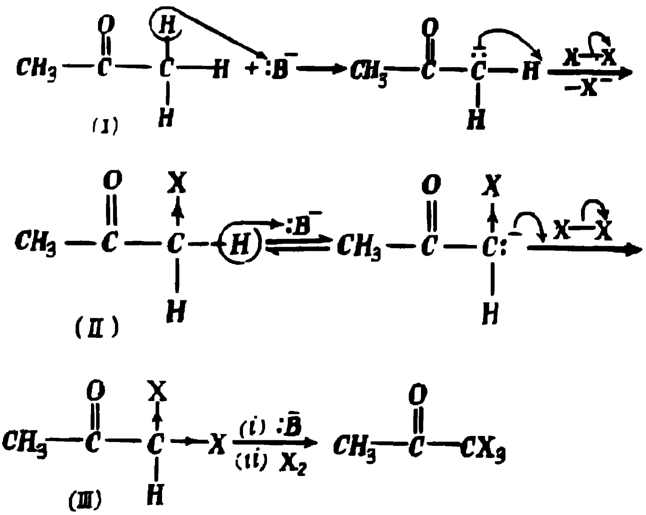
Enolization may be catalysed by acids or bases. In both cases acidity of the α-H atom plays an important role in the mechanism. The acidity of hydrogen atom in the α-position of the carbonyl group arises from *the electron withdrawing effect* of the carbonyl group and the stability of the enolate ion which results when a proton has been removed from the α-position.



$$-\overset{\alpha}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}- \underset{H_2O}{\overset{OH^-}{\rightleftharpoons}} \underset{\text{Enolate ion}}{\left[\,>\overset{\alpha}{\overset{}{C^-}}-C\overset{O}{\ll} \longleftrightarrow\ >C=C\overset{O^-}{<}\,\right]} \underset{OH^-}{\overset{H_2O}{\rightleftharpoons}} \underset{\text{enol}}{>\overset{\alpha}{C}=C\overset{OH}{<}}$$

The enolate ion is negatively charged and has a high electron density. The enol formed by protonation of the enolate on oxygen is also comparatively electron-rich around the α-carbon atom. Hence the enolate ion and the enol are both subject to electrophilic attack at this atom. Halogenation of ketones at the α-position is one reaction which depends on this reactivity. Haloform test for methyl ketones depends, among other things, on the same.

The Haloform Reaction. Acetone reacts with halogens in the presence of base (*i.e.*, in hypohalite solutions) when three hydrogen atoms of the methyl group are replaced by halogen atoms. Multiple halogenation occurs because on substitution of the first hydrogen by halogen atom, the remaining hydrogens on methyl carbon are more acidic through inductive effect of X atom. Thus H atom of CH_3 in I is acidic but the H atom of CH_2X in II is more acidic due to inductive effect of X atom. For the same reason H atom of CHX_2 in III is most acidic.



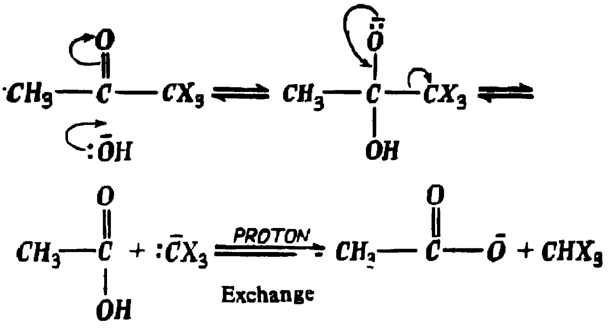
This is an example of base-promoted halogenation. Different steps involved are :

(*i*) Abstraction of a proton by the base :$\bar{B}$.

(*ii*) Electrophilic attack by the halogen at the negatively charged centre.

(*iii*) Repetition of the above two steps till all the three hydrogen atoms of the CH_3 group are replaced by three halogen atoms.

The trihaloacetone so obtained further reacts with aqueous alkali. The OH^- attacks the carbon atom of the trihaloacetone and causes a cleavage of the carbon-carbon bond between the carbonyl group and the trihalomethyl group. The ultimate products are the acetate ion and the haloform ($CHCl_3$, $CHBr_3$ or CHI_3)

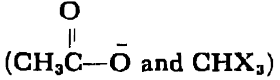


Various steps involved in the mechanism of the reaction are :

(*i*) Nucleophilic attack by $:\bar{O}H$.

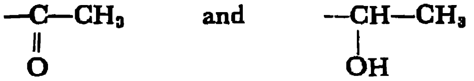
(*ii*) Adduct loses $:\bar{C}X_3$ to form acetic acid

(*iii*) Proton exchange to form a more stable pair



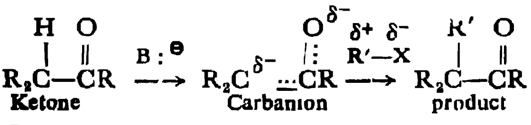
$(CH_3\overset{\overset{O}{\|}}{C}—\bar{O}$ and $CHX_3)$

The haloform reaction using iodine and aqueous NaOH is termed the idoform reaction. It is given by all compounds containing the two groups shown below :



$—\underset{\underset{O}{\|}}{C}—CH_3$ and $—\underset{\underset{OH}{|}}{CH}—CH_3$

(B) **Alkylation**. Rapid addition of a strong base (*e.g.*, ^-OR, $^-NH_2$, H^-) to an aldehyde or ketone gives the enolate ion which can react with R—X (wherein X is usually halogen or tosylate) to give an alkylated ketones or aldehyde.



Some Reactions of the Aldehydes not given by Ketones :

(1) **Polymerisation.** Aldehydes have a general tendency to polymerise, ketones do not polymerise.

Union of two or more molecules of a compound, without the elimination of a small molecule such as H_2O, NH_3 *or* CH_3OH, *etc., resulting in the formation of a new compound is called* **polymerisation.** Characteristics of the change are :

(*i*) It is a reversible change.

(*ii*) It is the union between molecules of the same compound without elimination of component elements.

(*iii*) No new carbon-to-carbon linkage is set up.

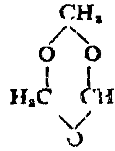
(*iv*) Molecular weight of the polymer is an exact multiple of the molecular weight of the original substance.

For example,

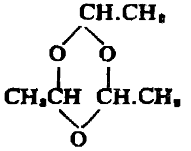
$$\underset{\substack{\text{Formaldehyde}\\(aq\ soln.)}}{n\mathrm{HCHO}} \xrightleftharpoons{\text{Evaporate}} \underset{\text{Para-formaldehyde}}{(\mathrm{CH_2O})_n}$$

$$\underset{\substack{\text{Formaldehyde}\\(aq.\ soln.)}}{3\mathrm{HCHO}} \xrightleftharpoons{\text{On standing}} \underset{\text{Meta-formaldehyde}}{(\mathrm{HCHO})_3}$$

$$\underset{\text{Acetaldehyde}}{3\mathrm{CH_3CHO}} \xrightleftharpoons{\text{conc. } \mathrm{H_2SO_4}} \underset{\text{Paraldehyde}}{(\mathrm{CH_3CHO})_3}$$

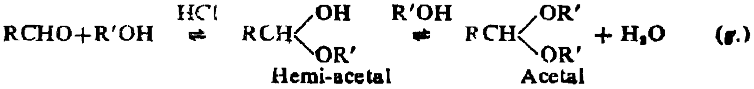


Meta-formaldehyde



Paraldehyde

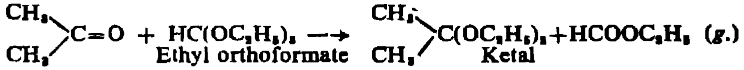
(2) **Acetal Formation.** In presence of dry hydrogen chloride gas aldehydes condense with alcohol to form first the *hemi-acetal* and then the *acetal*.



$$\mathrm{RCHO+R'OH} \xrightleftharpoons{\mathrm{HCl}} \underset{\text{Hemi-acetal}}{\mathrm{RCH}{<}\begin{matrix}\mathrm{OH}\\ \mathrm{OR'}\end{matrix}} \xrightleftharpoons{\mathrm{R'OH}} \underset{\text{Acetal}}{\mathrm{RCH}{<}\begin{matrix}\mathrm{OR'}\\ \mathrm{OR'}\end{matrix}} + \mathrm{H_2O} \quad (g.)$$

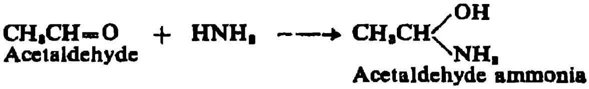
Acetals may be named as 1, 1-dialkoxyalkanes. They are stable compounds and are also stable in the presence of alkali. In presence of acid, however, parent aldehyde is regenerated. Acetal formation is used to protect the aldehyde group against alkaline oxidising agents while in acid solution it can be protected by mercaptal formation.

Ketones do not readily form *ketals* with alcohols. Ketals may, however, be obtained by treating the ketones with ethyl orthoformate.



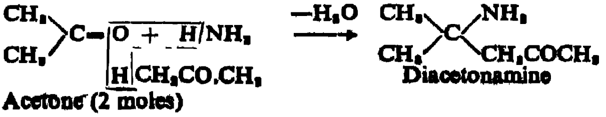
$$\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix}{>}\mathrm{C{=}O} + \underset{\text{Ethyl orthoformate}}{\mathrm{HC(OC_2H_5)_3}} \longrightarrow \underset{\text{Ketal}}{\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix}{>}\mathrm{C(OC_2H_5)_2}} + \mathrm{HCOOC_2H_5} \quad (g.)$$

(3) **Addition of Ammonia.** Aldehydes give an addition product called aldehyde ammonia while ketones give complex ketonic amines. Formaldehyde is an exception which gives hexamethylene tetramine.



$$\underset{\text{Acetaldehyde}}{\mathrm{CH_3CH{=}O}} + \mathrm{HNH_2} \longrightarrow \underset{\text{Acetaldehyde ammonia}}{\mathrm{CH_3CH}{<}\begin{matrix}\mathrm{OH}\\ \mathrm{NH_2}\end{matrix}}$$

$$\underset{\text{Formaldehyde}}{6\,\mathrm{HCH{=}O}} + 4\mathrm{NH_3} \longrightarrow \underset{\text{Hexamethylene-tetramine}}{(\mathrm{CH_2})_6\mathrm{N_4}} + 6\mathrm{H_2O}$$

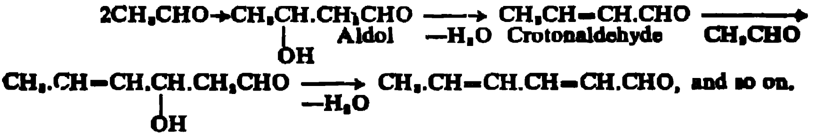


$$\underset{\text{Acetone (2 moles)}}{\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix}{>}\mathrm{C}{=}\begin{matrix}\boxed{\mathrm{O}\ +\ \mathrm{H}}\mathrm{NH_2}\\ \mathrm{H}\,\mathrm{CH_2CO.CH_3}\end{matrix}} \xrightarrow{-\mathrm{H_2O}} \underset{\text{Diacetonamine}}{\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix}{>}\mathrm{C}{<}\begin{matrix}\mathrm{NH_2}\\ \mathrm{CH_2COCH_3}\end{matrix}}$$

(4) **Action of Caustic soda.** Aldehydes give brown resinous mass with caustic soda, with ketones there is no action. Formaldehyde undergoes disproportionation when one molecule is reduced to methyl alcohol and the second one is oxidised to sodium formate (**Cannizzaro's Reaction**).

$$2HCHO + NaOH \rightarrow CH_3OH + HCOONa$$

The resin is probably formed *via* a series of condensation. For example, in the case of acetaldehyde

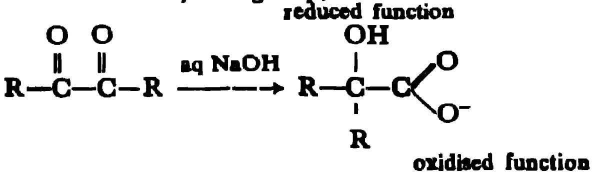


$$2CH_3CHO \rightarrow \underset{\text{Aldol}}{CH_3\underset{OH}{\underset{|}{C}H}.CH_2CHO} \xrightarrow[-H_2O]{} \underset{\text{Crotonaldehyde}}{CH_3CH{=}CH.CHO} \xrightarrow[CH_3CHO]{}$$

$$CH_3.CH{=}CH.\underset{OH}{\underset{|}{C}H}.CH_2CHO \xrightarrow[-H_2O]{} CH_3.CH{=}CH.CH{=}CH.CHO, \text{ and so on.}$$

For mechanism of Cannizzaro reaction *see* page 2·205.

Similar to Cannizzaro reaction is the **benzilic acid rearrangement** taking place when a diketone, $R-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-R$, is treated with aqueous NaOH. Here one of the R groups migrates and one of the $>C{=}O$ group is reduced to an alcohol while the other one is oxidised to carboxylate group, $-COO^-$



(5) **Tischenko Reaction.** All aldehydes can be made to undergo Cannizzaro's reaction by treatment with aluminium ethoxide. The alcohol and acid molecules so obtained react further to give an ester. For example, acetaldehyde gives ethyl acetate while propyl propionate is obtained from propionaldehyde.

$$\underset{\text{Acetaldehyde}}{2CH_3CHO} \xrightarrow{Al(OC_2H_5)_3} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5}$$

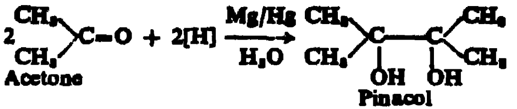
$$\underset{\text{Propionaldehyde}}{2C_2H_5CHO} \xrightarrow{Al(OC_2H_5)_3} \underset{\text{Propyl propionate}}{C_2H_5COOC_3H_7}$$

This modified Cannizzaro reaction is called *Tischenko reaction.*

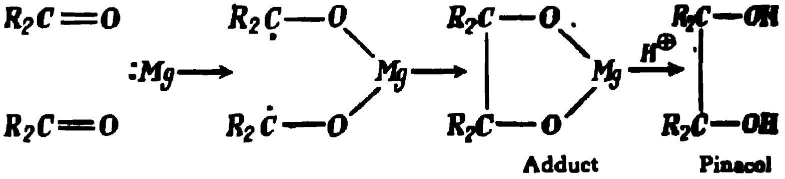
(6) **Schiff's Test.** Only aldehydes give a pink colour with Schiff's reagent (rosaniline hydrochloride solution in water decolorised with sulphur dioxide). The mechanism of the reaction is obscure.

Some Reactions of Ketones not given by Aldehydes :

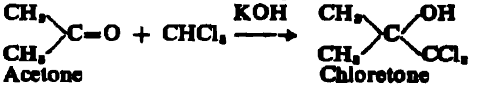
(1) **Bimolecular Reduction to Pinacols.** Ketones on reduction in acid solution or catalytically give secondary alcohols. When reduced in neutral or alkaline solution, pinacols are the main products. For example, acetone when reduced with magnesium algam forms pinacol.



Mechanism of the Reaction. Two electrons of :Mg form two covalent bonds with oxygen atoms of two $R_2C{=}O$ molecules leaving an unpaired electron with their two carbon atoms. These unpaired electrons form a covalent bond between two carbon atoms. The adduct on acidification forms a pinacol.



(2) **Condensation with Chloroform.** Ketones condense with chloroform in presence of caustic potash to form chlorohydroxy compounds. For example, acetone gives chloretone or chloro-butanol (1, 1, 1-Trichloro-2-methylpropan-2-ol),



5. Distinguishing Tests of Aldehydes and Ketones.—

Test	Aldehydes	Ketones
1. With Schiff's reagent.	Pink colour.	
2. With sodium hydroxide.	Brown resinous mass (Formaldehyde exception).	No change
3. With ammoniacal silver nitrate.	Silver mirror obtained.	No mirror obtained.
4. With Fehling's solution.	Red precipitate.	No precipitate.
5. With saturated sodium bisulphite solution, in water.	Crystalline bisulphite compounds with m.p. characteristic of the individual aldehydes.	Crystalline bisulphite compounds with m.p. characteristic of the individual ketones.
6. Warmed with hydroxylamine or phenylhydrazine.	Well-defined crystalline oximes and phenylhydrazones with m.p. characteristic of the individual aldehydes.	Well-defined crystalline oximes and phenylhydrazones with m.p. characteristic of the individual ketones.

SOME INDIVIDUAL MEMBERS

6. **Formaldehyde, Methanal, HCHO.**—It is the first member of the homologous series.

Preparation. Formaldehyde may be prepared using general methods of preparation of aldehydes discussed already. It is, however, prepared industrially :

(*i*) *By passing methanol vapour over heated copper at 570K.*

$$\underset{\text{Methanol}}{CH_3OH} \xrightarrow{Cu,\ 570K} \underset{\text{Formaldehyde}}{HCHO} + H_2$$

(*ii*) *By catalytic oxidation of Methanol.* Methyl alcohol vapours mixed with air passed over a copper or silver catalyst at 523-623K.

$$3CH_3OH+O_2 \longrightarrow 2HCHO+2H_2O$$

Presence of excess of air results in the further oxidation of formaldehyde to formic acid.

$$\underset{\text{Formaldehyde}}{2HCHO} + O_2 \longrightarrow \underset{\text{Formic acid}}{2HCOOH}$$

The amounts of methanol and air must, therefore, be carefully controlled.

The condensate obtained on condensing the vapours is a mixture of formaldehyde, methanol and water. Excess of methanol is removed by distillation and the resulting mixture called *formalin* contains 40 per cent formaldehyde, 8 per cent methanol and 52 per cent water.

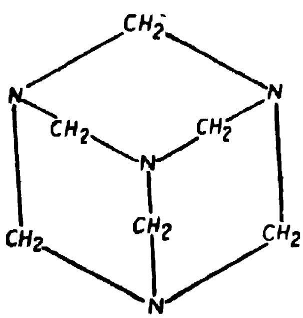
This very method is used for the *preparation of formalin in the laboratory.*

(*iii*) *By passing methane mixed with oxygen over a heated catalyst, e.g.,* molybdenum oxides.

$$CH_4+O_2 \rightarrow HCHO+H_2O$$

Properties : **Physical.** It is a colourless, pungent smelling gas readily soluble in water, alcohol and ether. It is a powerful disinfectant and antiseptic. When condensed, it yields a colourless liquid (b.p. 252K).

Chemical. The chemical properties of formaldehyde are the properties of the characteristic aldehyde group (—CH=O) present therein. With a few exceptions, as given below, its properties are the general properties of aldehydes.



Proposed structural formula for urotropine.

(*i*) *Reaction with Ammonia.* Formaldehyde reacts with ammonia to produce hexamethylenetetramine (urotropine—a drug used in disinfecting urinary canal).

$$6HCH=O+4NH_3 \longrightarrow \underset{\text{Hexamethylene-tetramine}}{(CH_2)_6N_4} + 6H_2O$$

Thus in this respect it differs from other aldehydes which produce aldehyde ammonia—an addition product with ammonia.

(*ii*) *Reaction with Sodium hydroxide.* Unlike other aldehydes which yield aldehyde resins with alkalis, formaldehyde undergoes **Cannizzaro's reaction.** Two molecules of formaldehyde react with one molecule of an alkali, when one molecule is reduced to methyl alcohol and the other is oxidised to formic acid.

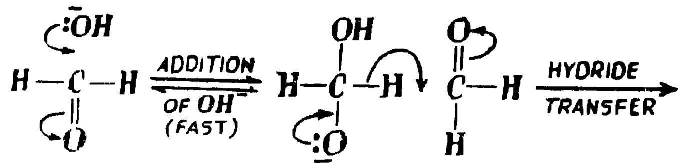
$$\underset{\text{Formaldehyde}}{2HCH{=}O} + \underset{\text{Potassium hydroxide}}{KOH} \longrightarrow \underset{\text{Methyl alcohol}}{CH_3OH} + \underset{\text{Potassium formate}}{HCOOK}$$

Mechanism of Cannizzaro Reaction. The reaction is believed to proceed in the following steps :

(i) Rapid, reversible addition of OH^- to one molecule of HCHO.

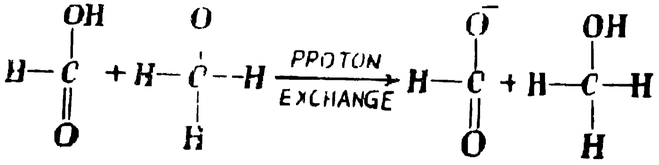
(ii) Transfer of hydride ion from the product obtained in (i) to second molecule of HCHO (*rate determining step*).

(iii) Formic acid and methoxide ion so obtained undergo a proton exchange to give a more stable pair CH_3OH and $HCOO^-$.



Formaldehyde (*first molecule*)

Formaldehyde (*second molecule*) (slow)



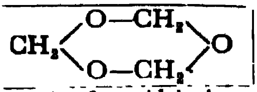
Formic acid Methoxide ion Formate ion Methyl alcohol

(*iv*) Formaldehyde is very useful for methylating primary and secondary amines. For example, with ethylamine it gives ethylmethylamine,

$$\underset{\text{Ethylamine}}{C_2H_5NH_2} + \underset{\text{Formaldehyde}}{2HCHO} \longrightarrow \underset{\text{Ethylmethylamine}}{C_2H_5NH.CH_3} + \underset{\text{Formic acid}}{HCOOH}$$

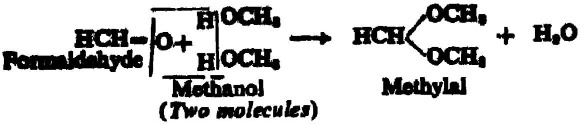
(*v*) *Polymerisation.* When formaldehyde solution (formalin) is evaporated to dryness, it polymerises to a white crystalline solid (m.p. 294-296K). The polymer is known as ***paraformaldehyde*** $(HCHO)_nH_2O$—n having values between 6 and 50. Paraformaldehyde forms formaldehyde again on heating.

On allowing formaldehyde gas to stand at room temperature, it slowly polymerises to metaformaldehyde, $(HCHO)_3$—a white solid (m.p. 334-335K). It does not show any reducing properties and is believed to have a cyclic structure as given in the margin.



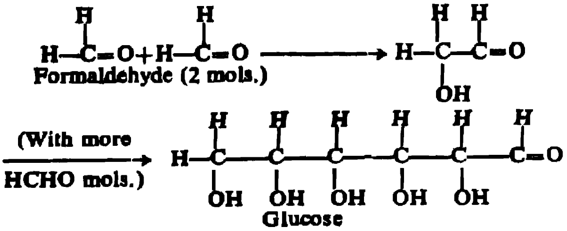
Metaformaldehyde
(A trimer)

(*v*) ***Reaction with Methanol.*** With methanol in presence of a dehydrating agent like dry hydrogen chloride gas or fused calcium chloride it yields methylal.



$$\underset{\text{Formaldehyde}}{HCH{=}O} + \underset{\substack{\text{Methanol}\\ \text{(Two molecules)}}}{\begin{matrix}H|OCH_3\\ H|OCH_3\end{matrix}} \longrightarrow \underset{\text{Methylal}}{HCH\begin{matrix}OCH_3\\ OCH_3\end{matrix}} + H_2O$$

(*vi*) *Aldol condensation.* Formaldehyde in the presence of a weak base undergoes repeated aldol condensations with elimination of water to give glucose.



$$\underset{\text{Formaldehyde (2 mols.)}}{H{-}CH{=}O + H{-}CH{=}O} \longrightarrow H{-}CH(OH){-}CH{=}O$$

$$\xrightarrow[\text{HCHO mols.)}]{\text{(With more}} \underset{\text{Glucose}}{H{-}CH(OH){-}CH(OH){-}CH(OH){-}CH(OH){-}CH(OH){-}CH{=}O}$$

(*vii*) *Condensation with Phenol.* Formaldehyde condenses with phenol, a hydroxy derivative of benzene, in the presence of a catalyst to yield bakelite (*a resin*).

Uses. Chief uses of formaldehyde which is available as formalin (40% solution) are :

(*i*) As antiseptic and germicide.

(*ii*) For preservation of biological and anatomical specimens.

(*iii*) In leather industry as a substitute for tanning as it can harden glue or gelatine and thus renders them insoluble in water.

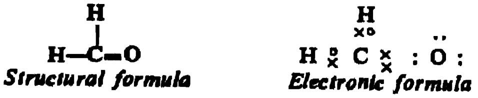
(*iv*) For the manufacture of formaldehyde resins—bakelite and galalith by catalytic condensation with phenol or casein (milk protein). The resin can be moulded while hot into different patterns under pressure.

(*v*) In the manufacture of synthetic dyestuffs.

Structure of Formaldehyde

(*i*) Molecular formula of formaldehyde as determined from its analytical data and molecular weight determination is CH_2O.

(*ii*) Assuming tetravalency of carbon, bivalency of oxygen and univalency of hydrogen, the only possible structural formula of formaldehyde is :



Structural formula *Electronic formula*

(*iii*) This agrees with all known properties of formaldehyde. The presence of an aldehyde group is confirmed by its analogy with acetaldehyde.

(iv) The two single C—H bonds are σ bonds while the C=O bond is a combination of one σ and one π bond. Carbon atom is in a state of sp^2 hybridisation. The three sp^2 hybrid orbitals are 120° apart and give three σ bonds by overlap with s orbitals of two hydrogen atoms and p orbitals of
1. π bond results from sideway overlap of p orbital of carbon with p
l of oxygen.

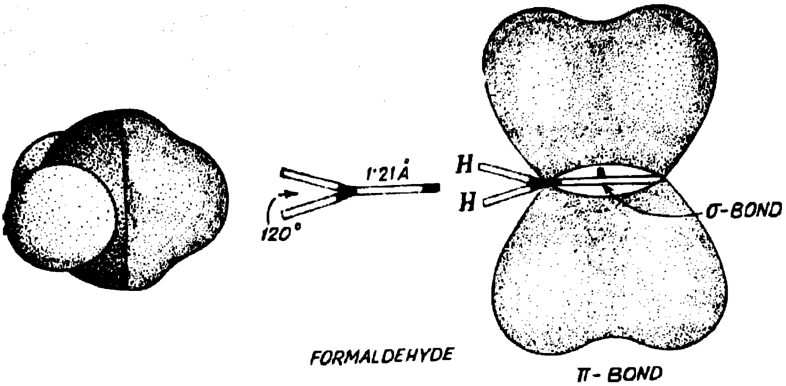


Fig. 22·1—Orbital representation of formaldehyde molecule.

7. Acetaldehyde, Ethanal, CH_3CHO.

Preparation. Acetaldehyde may be obtained by any of the general methods discussed already but it is usually prepared in the **laboratory by the oxidation of ethanol** with potassium dichromate and dilute sulphuric acid.

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$
$$\underset{\text{Ethanol}}{CH_3CH_2OH} + O \rightarrow \underset{\text{Acetaldehyde}}{CH_3CH{=}O} + H_2O$$

Expt. A mixture of powdered potassium dichromate (50 g) and water (200 ml) is placed in a round-bottom flask fitted with a dropping funnel and

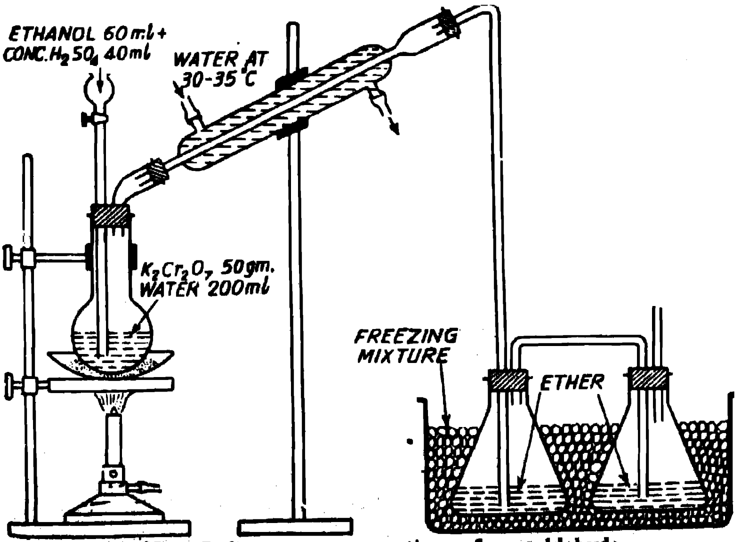
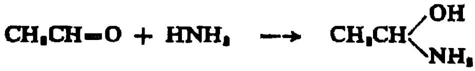
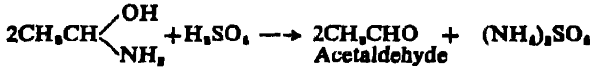


Fig. 22·2—Laboratory preparation of acetaldehyde.

water condenser (Fig. 22·2). A mixture of alcohol (60 ml) and conc sulphuric acid (40 ml) are placed in the dropping funnel and water at 303-308K is circulated through the water condenser. Flask is heated gently and the mixture from the dropping funnel is dropped slowly. Acetaldehyde vapours produced pass over and are bubbled through ether bottles dipped in freezing mixture. Any alcohol vapours accompanying acetaldehyde condense in water condenser and flow back. The solution of acetaldehyde in ether is saturated with ammonia when aldehyde ammonia crystals separate. These are removed, dried, decomposed with dilute sulphuric acid and distilled when acetaldehyde passes over at 294K.



$$CH_3CH{=}O + HNH_2 \longrightarrow CH_3CH\begin{cases}OH\\NH_2\end{cases}$$



$$2CH_3CH\begin{cases}OH\\NH_2\end{cases} + H_2SO_4 \longrightarrow 2CH_3CHO + (NH_4)_2SO_4$$

Aldehyde ammonia Acetaldehyde

Manufacture of Acetaldehyde. Acetaldehyde is prepared industrially

(*i*) **From Acetylene.** 42 per cent sulphuric acid, containing mercuric sulphate, is saturated at 330K with acetylene gas. On heating the mixture to 330-370K, acetaldehyde passes over and can be collected.

$$CH{\equiv}CH + H_2O \longrightarrow CH_3.CH{=}O$$

(*ii*) **By Catalytic Oxidation of Alcohol.** Alcohol vapours are mixed with air and passed over a silver catalyst at 523K when it is oxidised to acetaldehyde.

$$2C_2H_5OH + O_2 \longrightarrow 2CH_3CHO + 2H_2O$$

(*iii*) **By Dehydrogenation of alcohol.** Alcohol vapours are passed over heated copper at 570K when these are dehydrogenated to acetaldehyde.

$$CH_3CH_2OH \xrightarrow{Cu,\ 570K} CH_3CHO + H_2$$

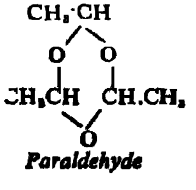
Properties of Acetaldehyde : Physical. It is a colourless, volatile liquid (b.p. 294K) with a characteristic pungent smell. It is lighter than water and miscible with water, alcohol and ether.

Chemical. Acetaldehyde is a typical member of the aldehyde series and gives all the general reactions of aldehydes given earlier.

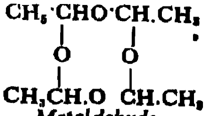
Polymers of Acetaldehyde. Acetaldehyde has a great tendency to polymerise.

(*i*) When treated with few drops of concentrated sulphuric acid, a vigorous reaction takes place and acetaldehyde polymerises to give the trimer *paraldehyde* $(CH_3CHO)_3$. It is a pleasant smelling liquid (b.p. 400K) used in medicine as hypnotic.

Acetaldehyde is regenerated when paraldehyde is distilled with dilute sulphuric acid. Paraldehyde has no reducing properties and is believed to have a ring structure as given below :



Paraldehyde



Metaldehyde

(*ii*) On treating acetaldehyde with a few drops of concentrated sulphuric acid at 273K, *Metaldehyde* $(CH_3CHO)_4$—tetramer is obtained. It is a white solid (m.p. 519K) used as solid fuel in spirit lamps. It regenerates acetaldehyde on distillation with dilute sulphuric acid. This is also believed to have a cyclic structure.

Uses of Acetaldehyde. It is used in the preparation of acetic acid, ethanol, butanol (a commercial solvent), paraldehyde, metaldehyde phenolic resins and synthetic drugs. Aldehyde ammonia is rubber accelerator. Acetaldehyde is also used in dye manufacture.

Tests. In addition to the test for aldehydes given before, acetaldehyde gives

(*i*) A blue colour when treated with sodium nitroprusside solution and piperidene.

(*ii*) A cherry-red colour when treated with freshly prepared sodium nitroprusside solution and excess of dilute caustic soda solution.

(*iii*) Iodoform reaction, as given by ethanol.

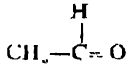
Structure of Acetaldehyde. (*i*) Molecular formula of acetaldehyde as deduced from its analytical data and molecular weight determination is C_2H_4O.

(*ii*) Acetaldehyde is obtained by oxidation of ethanol, and gives acetic acid on oxidation. Both ethanol and acetic acid contain a methyl group. We may reasonably assume that this methyl group remains intact during oxidation, and is, therefore, present in acetaldehyde also

$$\underset{\text{Ethanol}}{CH_3—CH_2OH} \xrightarrow{O} \underset{\text{Acetaldehyde}}{C_2H_4O} \xrightarrow{O} \underset{\text{Acetic acid}}{CH_3—COOH}$$

(*iii*) When treated with phosphorus pentachloride, acetaldehyde gives ethylidene chloride, $C_2H_4Cl_2$ and no hydrogen chloride is evolved in the reaction This implies the absence of a hydroxyl group and the presence of a divalent oxygen atom which is replaced by two monovalent chlorine atoms.

(*iv*) This gives the structural formula of acetaldehyde as :



$$CH_3—\overset{\overset{\large H}{|}}{C}=O$$

8. Chloral, Trichloroacetaldehyde, $CCl_3.CHO$.—

Preparation. *Chloral is prepared industrially by the chlorination of ethanol.* Chlorine is bubbled first into cooled ethanol and then at 333K till it is saturated. Chloral alcoholate is formed and separates as a crystalline solid. This is distilled with concentrated sulphuric acid to get chloral.

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[-2HCl]{Cl_2} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[-3HCl]{3Cl_2} \underset{\text{Chloral}}{CCl_3CHO}$$

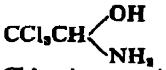
$$CCl_3.CHO + C_2H_5OH \longrightarrow \underset{\text{Chloral alcoholate}}{CCl_3.CH(OH).OC_2H_5}$$

$$\underset{\substack{\text{Chloral alcoholate}\\ (\textit{Crystalline solid})}}{CCl_3.CH(OH).OC_2H_5} + H_2SO_4 \longrightarrow \underset{\substack{\text{Chloral}\\ (\textit{Oily liquid})}}{CCl_3.CHO} + C_2H_5.HSO_4 + H_2O$$

The distillate is neutralised with calcium carbonate and redistilled.

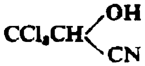
Properties : Physical. Chloral is a colourless, heavy, oily liquid (b.p. 371K) with a pungent odour. It is soluble in water, ethanol and ether.

Chemical. Chloral undergoes the usual reactions of an aldehyde, *e.g.*, it gives addition products with ammonia, hydrogen cyanide and sodium bisulphite.



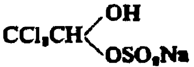
$CCl_3CH(OH)NH_2$

Chloral ammonia



$CCl_3CH(OH)CN$

Chloral cyanohydrin



$CCl_3CH(OH)OSO_2Na$

Bisulphite compound

With conc nitric acid it is oxidised to trichloroacetic acid.

$$CCl_3.CHO+O \xrightarrow{HNO_3} CCl_3\,COOH$$

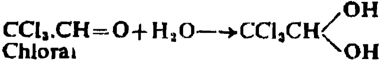
Some other reactions of chloral are :

(*i*) *Hydrolysis.* On heating with concentrated caustic potash, chloral gives pure chloroform.

$$CCl_3|\overline{CHO+KO}\,H \longrightarrow CHCl_3 + HCOOK$$

Chloral Chloroform

(*ii*) *With Water.* Its behaviour towards water is unusual When treated with water chloral reacts with the evolution of heat and yields chloral hydrate, $CCl_3.CH(OH)_2$—a stable crystalline compound (m.p. 330K).

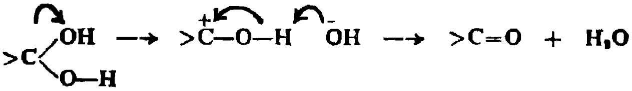


$$CCl_3.CH{=}O+H_2O \longrightarrow CCl_3CH(OH)_2$$

Chloral Chloral hydrate

Chloral hydrate is one of those unusual and rare compounds which are stable in spite of the fact that there are two hydroxyl groups attached to the same carbon atom.

The mechanism of the elimination of water from the $>C(OH)_2$ group is possibly as follows :

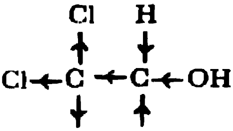


$$>C(OH)(O{-}H) \longrightarrow >\overset{+}{C}{-}O{-}H \quad \overset{-}{O}H \longrightarrow >C{=}O + H_2O$$

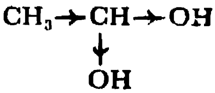
One of the two OH groups is released as the hydroxide ion, OH^-. This leaves the carbon atom positively charged and it attracts the electron pair of the C—O bond. This causes the oxygen atom to attract the electron pair of O—H bond and thereby facilitating the release of a proton which combines with OH^- to give a molecule of water. Thus a diol loses a molecule of water readily.

In chloral and other compounds of the formula $R.CX_2.CHO$, the carbon atom of the aldehyde group acquires small positive charge due to inductive effect of the halogen atoms. The positive charge on the carbon atom prevents the release of OH^- ion and no water is, therefore, eliminated.

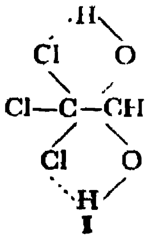
Another cause of stability of chloral hydrate molecule is the formation of intramolecular hydrogen bonds as shown in formula I below :



Chloral hydrate (*Does not lose a molecule of H_2O*)

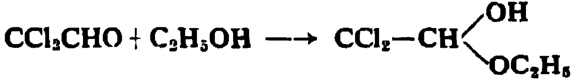


A diol (*Loses a molecule of H_2O*)



I

(*iii*) *With alcohol.* With alcohol combination takes place with the evolution of heat to give chloral alcoholate (m.p.320K).



$$CCl_3CHO + C_2H_5OH \longrightarrow CCl_2-CH\begin{matrix}OH\\ OC_2H_5\end{matrix}$$

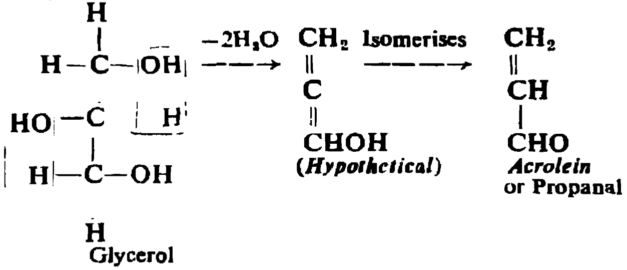
Chloral hydrate or chloral alcoholate are both stable compounds. Water or alcohol in them can, however, be removed by treatment with concentrated sulphuric acid.

(*iv*) *Polymerisation.* In the presence of acids, it polymerises to give metachloral, a white amorphous solid.

Uses. Chloral hydrate is used as a hypnotic (*sleep producing drug*) and as a powerful stimulant.

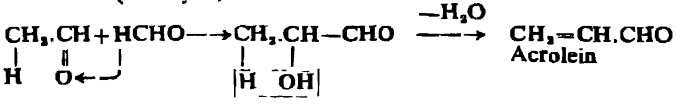
9. Acrolein, Acraldehyde, Prop-2 en-1-al, $CH_2{=}CA.CHO$.

Preparation. Acrolein is the simplest unsaturated aldehyde. It is conveniently prepared by the dehydration of glycerol with potassium hydrogen sulphate.



Commercially, acrolein is prepared as follows :

(*i*) *By passing a mixture of ethanal and methanal vapours over sodium silicate* (*catalyst*).



$$\underset{H}{CH_3.CH} + \underset{O}{HCHO} \longrightarrow \underset{H\quad OH}{CH_2.CH-CHO} \xrightarrow{-H_2O} CH_2{=}CH.CHO$$

Acrolein

(*ii*) *By direct oxidation of propylene over copper oxide.*

$CH_2{=}CH.CH_3 + O_2 \longrightarrow CH_2{=}CH.CHO + H_2O$

Properties. It is a colourless, pungent-smelling liquid (b.p. 325K). Its irritating smell causes watering of eyes and nose.

Chemically, it behaves like an olefin as well as an aldehyde as shown by its following reactions :

(*a*) *Reactions of the Double bond* (*olefinic linkage*). Acrolein gives addition products with halogens and halogen acids.

$CH_2{=}CH.CKO + Br_2 \longrightarrow CH_2Br.CHBr.CHO$

$CH_2{=}CH.CHO + HCl \longrightarrow CH_2Cl.CH_2.CHO$

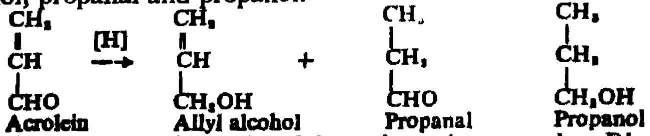
Addition of halogen acids occurs contrary to Markownikoff's rule (*cf.* allyl alcohol). Addition of HBr is unaffected by the presence of peroxides.

(*b*) *Reactions of the Aldehydic group.* Acrolein gives the usual reactions of aldehydes, *e.g.*,

(*i*) *Oxidation.* Ammoniacal silver nitrate oxidises acrolein to acrylic acid.

$$CH_2{=}CH.CHO + [O] \xrightarrow{\text{Am. AgNO}_3} CH_2{=}CH\ COOH$$

(*ii*) ***Reduction.*** On reduction acrolein gives a mixture of allyl alcohol, propanal and propanol.



$$\underset{\text{Acrolein}}{CH_2{=}CH{-}CHO} \xrightarrow{[H]} \underset{\text{Allyl alcohol}}{CH_2{=}CH{-}CH_2OH} + \underset{\text{Propanal}}{CH_3{-}CH_2{-}CHO} \quad \underset{\text{Propanol}}{CH_3{-}CH_2{-}CH_2OH}$$

(*iii*) ***Polymerisation.*** Acrolein polymerises to give ***Disacryl***—a white solid.

(*iv*) ***Tischenko reaction*** (*see* page 2·202).

$$2CH_2{=}CH.CHO \xrightarrow{(C_2H_5O)_3Al} \underset{\text{Allyl acrylate}}{CH_2{=}CH.COOCH_2.CH{=}CH_2}$$

(*v*) ***With Alkalis.*** Acrolein does not undergo aldol condensation with alkalis. The chain breaks at the double bond and we get a mixture of methanal and ethanal.

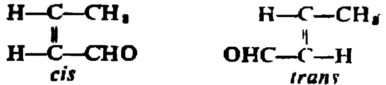
$$CH_2{=}CH.CHO + H_2O \xrightarrow{NaOH} HCHO + CH_3CHO$$

Uses. Acrolein finds use as tear gas and as a warning agent to find out leakage, if any, of methyl chloride used as a refrigerant.

10. Crotonaldehyde (2-Buten-1-al). $CH_3CH{=}CH\,CHO$ —It is prepared by heating aldol alone or with anhydrous zinc chloride or better still with acetic acid as catalyst.

$$CH_3CHOH.CH_2.CHO \xrightarrow{-H_2O} CH_3\,CH{=}CH\,CHO$$

It is a colourless liquid (b.p. 373K) and closely resembles acrolein in chemical properties. It exhibits geometrical isomerism and exists in *cis* and *trans* isomeric forms.

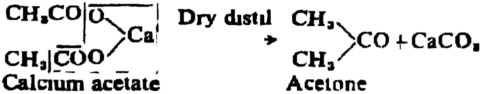


$$\underset{cis}{\begin{array}{c}H{-}C{-}CH_3\\ \|\\ H{-}C{-}CHO\end{array}} \qquad \underset{trans}{\begin{array}{c}H{-}C{-}CH_3\\ \|\\ OHC{-}C{-}H\end{array}}$$

Crotonaldehyde finds use as solvent, and as an insecticide.

11. Acetone, Dimethyl ketone or Propan-2-one, $CH_3.CO.CH_3$

Laboratory Preparation. Acetone is prepared in the laboratory by dry distillation of fused calcium acetate.



$$\underset{\text{Calcium acetate}}{\begin{array}{l}CH_3CO{-}O\\ \qquad\qquad\;\; \rangle Ca\\ CH_3{-}COO\end{array}} \xrightarrow{\text{Dry distil}} \underset{\text{Acetone}}{\begin{array}{l}CH_3\\ \quad\;\rangle CO\\ CH_3\end{array}} + CaCO_3$$

Expt. About 30–40 grams of fused calcium acetate is powdered and taken in a retort fitted with Liebig's condenser and a receiver as shown (Fig. 22·3). The retort is heated over a wire gauze when acetone distils over.

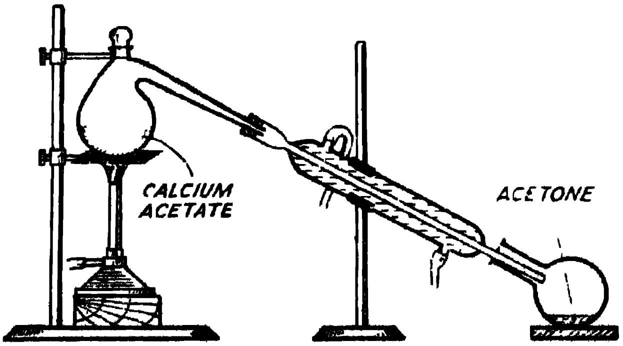
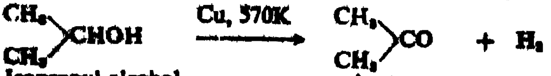


Fig. 22·3—Preparation of acetone in the laboratory.

This distillate is shaken with a saturated solution of sodium bisulphite when crystals of the bisulphite compound of acetone are obtained. These are filtered off and decomposed by distillation with a saturated solution of sodium bicarbonate. The aqueous solution of acetone obtained is dried over fused calcium chloride and redistilled.

Manufacture. Acetone is prepared industrially :

(*i*) *By passing isopropyl alcohol vapours over heated copper at 570K.*



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CHOH \xrightarrow{Cu,\ 570K} \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CO + H_2$$

Isopropyl alcohol Acetone

(*ii*) *By passing acetic acid vapour over a catalyst (calcium oxide or manganous oxide) at 570-670K.*

$$CH_3CO\boxed{OH + H}\ \boxed{OOC}\,CH_3 \xrightarrow{MnO} CH_3.CO.CH_3 + CO_2 + H_2O \qquad (i)$$

Acetic acid (*Two molecules*) Acetone

(*iii*) *By passing a mixture of ethyl alcohol vapour and steam over a catalyst, zinc chromite at 770K.* The yield is about 80 per cent.

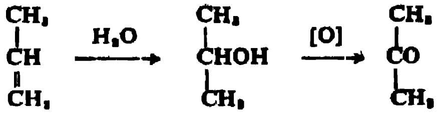
$$\underset{\text{Ethanol}}{2C_2H_5OH} + \underset{\text{Steam}}{H_2O} \xrightarrow[770K]{Zn(CrO_2)_2} \underset{\text{Acetone}}{CH_3CO.CH_3} + CO_2 + 4H_2$$

(*iv*) *By fermentation of molasses or cooked corn starch* (*Weizmann process, 1911*). Starch or molasses is fermented with the micro-organism, *clostridium acetobutylicum*. Carbon dioxide and hydrogen are evolved during the reaction. The products of reaction are butanol, acetone and ethanol approximately in the ratio 6 : 3 : 1. These are separated and purified by distillation. This method is, however, being replaced by the synthetic method given above.

Some newer processes *for the manufacture of acetone are* :

(*i*) *By passing a mixture of acetylene and steam over heated pure zinc oxide* (*catalyst*).

(*ii*) *By heating under pressure a mixture of propylene and steam in the presence of a suitable catalyst.*



$$\begin{matrix}CH_3\\|\\CH\\\|\\CH_2\end{matrix} \xrightarrow{H_2O} \begin{matrix}CH_3\\|\\CHOH\\|\\CH_3\end{matrix} \xrightarrow{[O]} \begin{matrix}CH_3\\|\\CO\\|\\CH_3\end{matrix}$$

(*iii*) *By oxidation of natural gas* under carefully controlled conditions when a complex mixture of compounds, *e.g.*, HCHO, CH_3CHO, $(CH_3)_2CO$, CH_3COOH and alcohols is obtained.

Properties of Acetone : Physical. Acetone is a colourless, pleasant-smelling liquid (b.p. 328K). It is miscible with water, ethanol and ether in all proportions.

Chemical. Acetone is a typical member of ketone family. Its reactions are given under general reactions of ketones.

Uses of Acetone. (*i*) As a solvent for cellulose acetate and nitrate, celluloid, lacquers, etc.

(*ii*) For storing acetylene.

(*iii*) In the manufacture of sulphonal—a soporific and ionone—an artificial scent.

(*iv*) In the manufacture of cordite—a smokeless powder.

Tests for Acetone. In addition to the tests already given for ketones in general, a few particular tests for acetone are :

(*i*) *Iodoform Test.* Ammonia is added to iodine solution until slightly brown. This is warmed with acetone when iodoform is formed and crystallizes on cooling. *Ethanol gives iodoform with caustic soda, not ammonia.*

(*ii*) *Legal's Test.* Freshly prepared solution of sodium nitroprusside is added to a dilute solution of acetone. Caustic soda solution is then added drop by drop when an orange colour is obtained and changes to yellow on standing.

These tests are, however, given by any ketone with CH_3CO—group.

Structure of Acetone. (*i*) Molecular formula of acetone as determined from its analytical data and molecular weight determination is C_3H_6O.

(*ii*) With phosphorus pentachloride acetone gives isopropylidene chloride, $C_3H_6Cl_2$ and no hydrogen chloride. This shows the absence of a hydroxyl group and implies the presence of a carbonyl group whose bivalent oxygen is replaced by two univalent chlorine atoms.

(*iii*) Assuming quadrivalency of carbon, bivalency of oxygen and univalency of hydrogen, the two possible structures of acetone are :

$$\underset{\text{I}}{CH_3.CH_2.CHO} \qquad \underset{\text{II}}{CH_3.CO.CH_3}$$

(*iv*) Formula I contains the aldehydic group, and acetone does not behave like an aldehyde. II must, therefore, be the structural formula of acetone.

(*v*) This is further confirmed by all the known reactions of acetone.

12. Ethyl methyl ketone, 3-Butanone, $CH_3.CO.C_2H_5$.—It can be prepared by any of the general methods but can be manufactured :

(*i*) *By passing butanol-2 vapour over copper at 570K.*

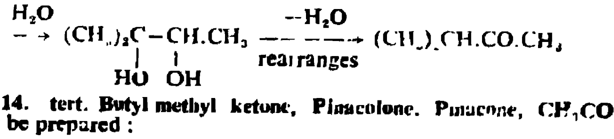
$$CH_3.CHOH\ CH_2\ CH_3 \longrightarrow CH_3CO.CH_2CH_3+H_2$$

(*ii*) *By oxidation of 2-butanol with air using silver catalyst at 520K.*

$$2CH_3.CHOH.CH_2.CH_3+O_2 \longrightarrow 2CH_3CO.CH_2.CH_3+2H_2O$$

It is a pleasant-smelling liquid (b.p. 353K). It is used as a solvent for vinyl resins, synthetic rubber, etc.

13. Methyl isopropyl ketone, 3-Methylbutan-2-one CH_3 CO.CH(CH$_3$)$_2$. Out of the several ways available for its preparation, the best one is by treating tert. amyl alcohol with bromine and hydrolysing the dibromo derivative whereupon it is formed as a result of a molecular rearrangement (*see* pinacone below).

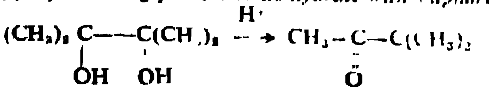


$$(CH_3)_2COH.CH_2.CH_3 \xrightarrow{Br_2} (CH_3)_2CBr.CHBr.CH_3$$

$$\xrightarrow{H_2O} (CH_3)_2\underset{\text{HO}}{\underset{|}{C}}-\underset{\text{OH}}{\underset{|}{C}}H.CH_3 \underset{\text{rearranges}}{\xrightarrow{-H_2O}} (CH_3)_2CH.CO.CH_3$$

14. tert. Butyl methyl ketone, Pinacolone. Pinacone, $CH_3CO.C(CH_3)_3$.—It may be prepared :

(*i*) *By distilling pinacol or its hydrate with sulphuric acid.*

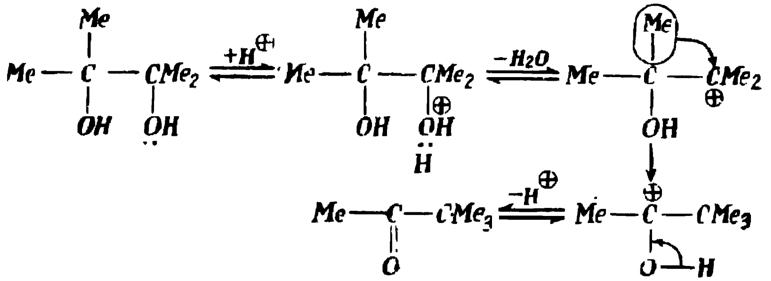


$$(CH_3)_2\underset{\text{OH}}{\underset{|}{C}}-\underset{\text{OH}}{\underset{|}{C}}(CH_3)_2 \xrightarrow{H^+} CH_3-\underset{\text{O}}{\underset{\|}{C}}-C(CH_3)_3 \qquad (65\text{-}72\%)$$

Pinacol Pinacone

(*ii*) *By passing pinacol dissolved in dioxan over heated catalyst (silica gel impregnated with H_3PO_4). The yield is about 94%.*

This conversion of pinacol into pinacone is an example of 1, 2-shift and is termed **pinacol-pinacone rearrangement.**



It is a colourless liquid (b.p. 392K) with a camphor-like odour. It is oxidised to trimethylacetic acid with alkaline sodium hypobromite.

$$CH_3.CO.C(CH_3)_3 \xrightarrow{Br_2/NaOH} (CH_3)_3C.COOH \qquad (71\text{-}74\%)$$

15. Methyl vinyl ketone, 3-Buten-2-one, $CH_3.CO.CH{=}CH_2$.—It may be prepared :

(*i*) By aldol condensation between formaldehyde and acetone followed by dehydration of the product.

$$HCHO+CH_3.CO.CH_3 \xrightarrow{NaOH} CH_2OH.CH_2.CO.CH_3 \xrightarrow{-H_2O} CH_2{=}CH.CO.CH_3$$

(*ii*) By the action of acetic anhydride on ethylene in presence of $ZnCl_2$ (*catalyst*).

$$CH_2{=}CH_2+(CH_3CO)_2O \xrightarrow{ZnCl_2} CH_2{=}CH.CO.CH_3+CH_3COOH$$

(*iii*) By the action of acetic anhydride on vinyl magnesium bromide in tetrahydrofuran at 200-210K.

$$2CH_2{=}CH.MgBr+2(CH_3CO)_2O \longrightarrow 2CH_2{=}CH.COCH_3+MgBr_2 + (CH_3COO)_2Mg \quad (60\text{-}80\%)$$

It is manufactured by hydrating vinylacetylene in the presence of dilute sulphuric acid and mercuric sulphate.

$$CH_2{=}CH.C{\equiv}CH + H_2O \longrightarrow CH_2{=}CH.CO.CH_3$$

It is a liquid (b.p. 352K) which polymerises on standing. It is used as starting material in the manufacture of plastics.

16. Mesityl oxide, 4-Methyl-3-penten-2-one, $(CH_3)_2C{=}CH.CO.CH_3$.—It is prepared : (*i*) By distilling diacetone alcohol with a trace of iodine.

$$(CH_3)_2C(OH).CH_2.CO.CH_3 \xrightarrow{-H_2O} (CH_3)_2C{=}CH.CO.CH_3 \qquad (90\%)$$

(*ii*) From isobutylene.

$$(CH_3)_2C{=}CH_2+CH_3COCl \xrightarrow{ZnCl_2} (CH_3)_2CCl.CH_2.CO.CH_3 \xrightarrow{-HCl} (CH_3)_2C{=}CH.CO.CH_3$$

It is liquid (b.p. 375K) having a peppermint smell and finds use as a solvent for oil, gums, etc.

17. Phorone, 2, 6-dimethyl-2, 5-heptadien-4-one, $(CH_3)_2C{=}CH.CO.CH{=}C(CH_3)_2$.—It may be prepared by the action of HCl on acetone (*see* page 2·198). It is a yellow crystalline solid (m.p. 301, b.p. 471K).

QUESTIONS

Essay Type :

1. Give the general methods for the preparation of aldehydes and ketones and describe the general properties of these two groups of compounds. In what ways is formaldehyde abnormal ?

2. Compare and contrast the properties of acetaldehyde and acetone. Give equations of the reactions. (*Delhi B.Sc. 1972*)

3. What are the properties common to aldehydes and ketones ? What are their differences ? (*Delhi B.Sc. Hons. Sub. 1977*)

4. Give preparation, properties and uses of acetaldehyde. (*Jammu B.Sc. 1975*)

5 Give at least four general methods for preparation of ketones. In what respects do they differ from aldehydes ?
(*Delhi B.Sc. Hons. Sub. 1976 Supp.* ; *Punjabi 1976*)

6. Explain any two methods for the manufacture of acetone. What happens when acetone is (*a*) reduced, (*b*) oxidised, (*c*) treated with PCl_5 ?
(*Delhi B.Sc. Hons. Sub. 1976* ; *Madras B.Sc. 1976*)

7. How is formaline prepared ? Give its properties and uses. (*Jammu B.Sc. 1977*)

8. How is chloral prepared ? What are its properties and uses ? (*Delhi B.Sc. 1976 Supp.*)

9. How will you proceed to get :

(*i*) Acetaldoxime, (*ii*) Acetone hydrazone

(*iii*) Benzaldehyde bisulphite, and

(*iv*) Aldol from the corresponding aldehydes or ketones. Give the mechanism of the reactions you choose. (*Guru Nanak Dev B.Sc. 1977*)

10. How is acrolein prepared ? State its important properties and uses.

11. (*a*) Suggest one method of synthesis of (*i*) di-isopropyl ether, (*ii*) vinylm ethyl ketone.

(*b*) Give the steps in the conversion of 3-methyl-1-butene to isobutyraldehyde.

(*c*) Give acceptable explanation for the observation that the carbonyl group in carboxylic acids does not react with phenylhydrazine. (*Delhi B.Sc. Hons. 1971*)

12. (*a*) Give the electronic mechanism of the following :

(*i*) Addition of HCN and $NaHSO_3$ to carbonyl group.

(*ii*) Aldol condensation.

(*b*) Explain the following :

(*i*) Acetone is less reactive than acetaldehyde.

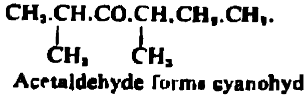
(*ii*) Hydrogan atom of the carboxyl group is more readily replaced than hydrogen atom of alcoholic group.

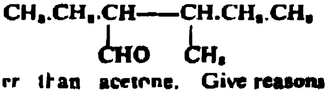
(*iii*) The carbonyl group in an acid is rather inert and does not show usual reaction of carbonyl group in aldehydes and ketones.
(*Guru Nanak Dev B.Sc. 1971*)

13 Write names of the following :

(*i*) $(CH_3)_2CH.CHO$ (*ii*) $CH_3.CH_2.COCH_2.CH_3$.

(*iii*) $CH_3.CH_2.CH_2.CH_2.CO.CH_3$. (*iv*) $CH_3.CHCl.CO.CH_2.CH_2Cl$

(*v*) 
$$CH_3.\underset{CH_3}{\underset{|}{CH}}.CO.\underset{CH_3}{\underset{|}{CH}}.CH_2.CH_3.$$

(*vi*) 
$$CH_3.CH_2.\underset{CHO}{\underset{|}{CH}}—\underset{CH_3}{\underset{|}{CH}}.CH_2.CH_3$$

14. Acetaldehyde forms cyanohydrin faster than acetone. Give reasons. (*Mudurai B.Sc. 1976*)

15. Starting from acetone how will you obtain :

(*a*) *t*-butyl alcohol, (*b*) Isopropyl bromide,

(*c*) tetramethylene glycol, (*d*) chloroform, and

(*e*) Mesitylene ? (*Mudurai B.Sc. 1976*)

16. Discuss the structure of carbonyl group.

17. Discuss any three nucleophilic addition reactions of aldehydes and ketones.

Short Answer Type :

1. How do you account for high dipole moment of aldehyde and ketones ?

2. Write IUPAC names of the compounds whose formulae are given below :

(*i*) C_6H_5CHO (*ii*) $CH_3CH_2COCH_2CH_3$

(*iii*) $CH_3.C_6H_4.CHO$ (*iv*) $CH_3COCH_2CH_3$

3. Write the formulae of various carbonyl compounds having the molecular formula C_4H_8O and give their trivial as well as IUPAC names.

4. How is an aldehyde obtained from an acid chloride ?

5. How is ketone obtained from an acid chloride ?

6. In what respect is dialkylcadmium superior to Grignard reagent for the preparation of a ketone from an acid chloride ?

7. Solubility of carbonyl compounds decreases with the increase in their molecular masses. Explain why ?

8. Boiling points of aldehydes lie between parent alkanes and corresponding alcohols. How do you account for it ?

9. What do you understand by nucleophilic addition to the carbonyl group ? Write mechanism.

10. How do you represent and account for acid-catalysed nucleophilic addition to the carbonyl group ?

11. Write mechanism for the nucleophilic addition of HCN and $NaHSO_3$ to $>C=O$ group.

12. What is aldol condensation ?

13. What is Tollen's reagent ? How does it react with acetaldehyde ?

14. Write a short note on :

(*i*) Clemmensen reduction. (*ii*) Wolff-Kishner reduction.

(*iii*) Meerwein-Ponndorf reduction.

15. How do you account for the following :

(*a*) In the laboratory preparation of acetaldehyde by oxidation of ethanol, acetaldehyde is distilled out continuously.

(*b*) Dialkylcadmium is considered superior to Grignard reagent for the preparation of a ketone from an acid chloride.

(*c*) $NaHSO_3$ is used for the purification of aldehydes and ketones.

16 Write two reactions showing difference between HCHO and CH_3CHO.

17. Give two chemical properties in which CH_3CHO and CH_3COCH_3 differ.

18 Give chemical tests to distinguish between acetaldehyde and acetone. (*Delhi B.Sc. 1976*)

19. What happens when acetaldehyde is treated with dilute sodium hydroxide solution ? (*Delhi B.Sc. 1976*)

20. Write a short note on aldol condensation. (*Delhi B Sc. 1973, 77 ; B Sc. Hons. Sub. 1976 ; Kerala 1976*)

21. Explain briefly why chloral forms stable hydrate. (*Delhi B.Sc. Hons. 1976*)

22. Write equation to show Cannizzaro's reaction. (*Delhi B Sc. 1976*)

23. Explain intermolecular hydride transfer in Cannizzaro reaction. (*Delhi B.Sc. Hons. 1976*)

24. Write a note on addition reactions of carbonyl group. (*Delhi B Sc. Hons. Sub. 1977*)

25. CH_3COCH_3 reacts with phenylhydrazine but CH_3CONH_2 does not, though both have the carbonyl group. Explain why ? (*Kerala B.Sc. 1975*)

26. Discuss the mechanism of pinacol-pinacolone rearrangement. *(Delhi B.Sc. Hons. 1976 ; Nagpur B.Sc. 1974 Supp.)*

27. Why does acetaldehyde not undergo Cannizzaro reaction ? *(Delhi B.Sc. Hons. 1977)*

28. Why do aldehydes and ketones have high dipole moments ? *(Guru Nanak Dev B.Sc. 1977)*

29. Write a short note on Rosenmund's reaction. *(Madras B.Sc. 1976)*

30. How may acetone be obtained from acetic acid ? *(Madras B.Sc. 1978)*

31. How does

(*i*) hydroxylamine react with acetaldehyde ?

(*ii*) formaldehyde react with ammonia ? *(Madras B.Sc. 1978)*

32. What is aldol condensation ? *(Madras B.Sc. 1978)*

33. Indicate the method of converting acetone into

(*i*) chloroform, (*ii*) mesitylene,

(*iii*) isopropyl acohol, (*iv*) α-hydroxy-isobutyric acid. *(Madras B.Sc. 1978)*

34. How may acetaldehyde be converted into lactic acid ? *(Madras B.Sc. 1978)*

35. Give the structural formulae of the following compounds and describe the type of hybridisation of the carbon in them.

(*i*) actone, (*ii*) acetaldehyde, (*iii*) 2-pentanone. *(Osmania B.Sc. 1979)*

36 Cyclohexanone and cyclohexanol are both liquids insoluble in water and with similar boiling points. How can you remove traces of cyclohexanone present in cyclohexanol ?

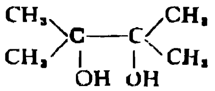
Hints : Dissolve in ether and shake with $NaHSO_3$ (aqueous solution) Bisulphite adduct of cyclohexanone dissolves in aqueous layer. Separate ether layer, dry and distil off ether.

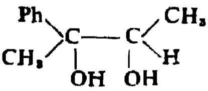
37. How can you convert 4 pentenal (*i*) to pentanal and (*ii*) to 4-penten-1-ol ?

Hints : (*i*) Use H_2(Pt) catalytic hydrogenation of C=C bond is faster than C=O bond.

(*ii*) Use $NaBH_4$ in water which reduces C=O bond but does not reduce C=C bond.

38. How are the following pinacols prepared ?

(*i*)


(*ii*)


What happens when the pinacol (*ii*) is heated with acid ? Give the mechanism of the reaction. *((Delhi B.Sc. Hons. 1981)*

39 Justify the statement that the Cannizzaro reaction involves an intermolecular shift of hydrogen as hydride ion. Give a suitable example, *(Delhi B.Sc. Hons. 1981)*

Problems :

1. An organic compound **A** with molecular formula C_3H_6O is not readily oxidised. It gives on reduction C_3H_8O (**B**) which reacts with HBr to give a bromide **C**. Grignard reagent obtained from **C** reacts with **A** to give $C_6H_{14}O$ (**D**) Identify the compounds from **A** to **D**.

2. An organic compound **A** with molecular formula C_3H_6O is oxidised by Fehling's solution and gives silver mirror with Tollen's reagent. **A** gives on reduction C_3H_8O (**B**). With hydrobromic acid followed by heating with magnesium **B** gives C which reacts with ethylene oxide to give $C_5H_{12}O$ (**D**). On oxidation **D** gives $C_5H_{10}O_2$ (E). Identify the compounds **A** to **E**.

3. An organic compound **A** on analysis was found to contain : C=16·271%. H=0·677%. and Cl=72·203%.

(*a*) It reduced Fehling's solution and on oxidation gave a monocarboxylic acid **B** having C=14·679%, H=0·612% and Cl=65·137%.

(*b*) On distillation with sodalime, B gave a sweet smelling liquid C containing 89·12% chlorine and which can also be obtained by heating A with alkali.

(*c*) A can also be obtained by action of Cl_2 on ethyl alcohol. Assign structure to, A, B, C and explain the reactions.

4. An organic compound A containing 40% carbon, 6·6% hydrogen and vapour density 15 restores the colour of Schiff's reagent. On treatment with caustic potash it gave an alcohol B that could be obtained on reduction of A. What was the compound A ? Explain the reactions.

5. A compound X contains C=69·77%, H=11·63%. Its V.D. is 43. Among the products of oxidation, the two monobasic acids M and N can be recognized. M had the empirical formula $C_3H_6O_2$. Its ethyl ester has vapour density of 51. N has the simplest formula CH_2O. Its ethyl ester has vapour dedsity of 44. From these data, deduce the possible structures for X.

6. An organic compound contains C=69·77% and H=11·63%. Its vapour density is found to be 43. It gave a crystalline derivative with sodium bisulphite, but did not reduce Fehling's solution. On oxidation it gave a mixture of acetic acid and propionic acid. Deduce its possible structures.

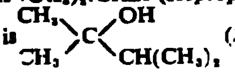
7. 0·1588 g of an organic substance gave 0·3615 g of CO_2 and 0·1479 g of H_2O. Its V.D. was 29. The compound reduces Fehling's solution and on oxidation gave an acid, the silver salt of which contained 95·6% Ag. Give the name and structural formula of the compound.

8. Two isomeric neutral substances A and B contained 62·01% carbon and 10·35% H. Their vapour density is 29. On mild oxidation A gives rise to monobasic acid C containing 48·64% carbon and 1·11% H. The equivalent weight of C is 74. On similar treatment B remains unaffected but it readily reacts with iodine and sodium hydroxide producing iodoform. What are the structural formulae of A and B ?

9. 0·29 g of an organic compound containing carbon, hydrogen and oxygen yield 0·66 g of carbon dioxide and 0·27 g of water. The vapour density of the compound was 29. What substances correspond to these data and how would you distinguish between them ? Suggest one method for synthesising each.

ANSWERS

1. A is $CH_3.CO.CH_3$ (*Acetone*) ; B is $(CH_3)_2.CHOH$ (*Isopropyl alcohol*) ; C is $(CH_3)_2.CHBr$ (*Isopropyl bromide*).

D is  (*2 : 3-Dimethyl-2-butanol*)

2. A is CH_3CH_2CHO (*Propionaldehyde*)

B is $CH_3.CH_2CH_2OH$ (*n-Propyl alcohol*)

C is $CH_3.CH_2.CH_2.MgBr$ (*n-Propylmagnesium bromide*)

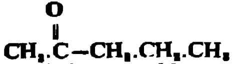
D is $CH_3CH_2.CH_2CH_2CH_2OH$ (*1-Pentanol*)

E is $CH_3CH_2CH_2.CH_2.COOH$ (*Pentanoic acid*)

3. A is $CCl_3.CHO$ (*Chloral*) ; B is $CCl_3.COOH$ (*Trichloroacetic acid*) ; C is $CHCl_3$ (*Chloroform*).

4. A is HCH=O (*Formaldehyde*)

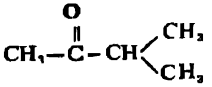
5. The possible isomers are :



$CH_3.\overset{O}{\overset{\|}{C}}-CH_2.CH_2.CH_3$

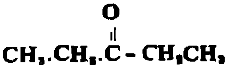
Methyl *n*-propyl ketone

(I)



Methyl *iso*-propyl ketone

(II)



$CH_3.CH_2.\overset{O}{\overset{\|}{C}}-CH_2CH_3$

Diethyl ketone

(III)

6. Mol. formula = $C_5H_{10}O$

Possible structures : $CH_3.CO.CH_2.CH_2.CH_3$; $C_2H_5.CO.C_2H_5$

Methyl *n*-propyl ketone ; Diethyl ketone

Methyl isopropyl ketone is ruled out since it does not yield acetic acid and propionic acid on oxidation.

7. C_2H_5CHO (*Propionaldehyde*)

8. A is C_2H_5CHO (*Propionaldehyde*) ; B is $CH_3.CO.CH_3$ (*Acetone*)

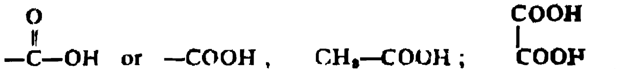
9. C_2H_5CHO ; $CH_3.CO.CH_3$; and $CH_2=CH.CH_2OH$

Propionaldehyde ; Acetone ; (*Allyl alcohol*)

23

Monocarboxylic Acids

1. **Carboxylic Acids.**—Organic compounds which contain one or more carboxyl groups, —COOH, have acidic properties and are called carboxylic acids. The word carboxyl is a contraction of the words **carbonyl** (C=O) and **hydroxyl** (OH) as in the carboxyl group the C=O and (OH) groups are combined as shown below :

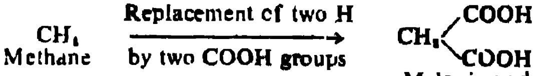


$$\overset{\displaystyle O}{\overset{\|}{-C}}-OH \text{ or } -COOH\text{ ,}\quad CH_3-COOH\text{ ;}\quad \begin{array}{c}COOH\\|\\COOH\end{array}$$

Carboxyl group Acetic acid Oxalic acid

The carboxylic acids may be considered as carboxyl derivatives of hydrocarbons in which one or more hydrogen atoms are replaced by carboxyl groups, *e.g.*,

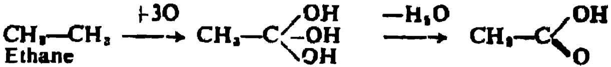
$$\underset{\text{Methane}}{CH_4} \xrightarrow[\text{by one COOH group}]{\text{Replacement of one H}} \underset{\text{Acetic acid}}{CH_3.COOH}$$



$$CH_4 \xrightarrow[\text{by two COOH groups}]{\text{Replacement of two H}} CH_2\begin{matrix}\diagup COOH\\ \diagdown COOH\end{matrix}$$

Methane Malonic acid

We may also view at them as oxidation products of hydrocarbons in which one —CH_3 group is replaced by one —COOH group, *e.g.*,



$$CH_3-CH_3 \xrightarrow{+3O} CH_3-C\begin{matrix}\diagup OH\\ -OH\\ \diagdown OH\end{matrix} \xrightarrow{-H_2O} CH_3-C\begin{matrix}\diagup OH\\ \diagdown\!\!\diagdown O\end{matrix}$$

Ethane Oxidation product (*unstable*) Acetic acid

Acids containing *one* COOH group are termed *mono*-carboxylic acids while others containing *two* and *three* COOH groups are called *di*- and *tri*- carboxylic acids respectively.

2. **Fatty Acids.**—The monocarboxylic acids are called *fatty acids*. The name arose from the fact that some of the higher members, *e.g.*, palmitic acid ($C_{15}H_{31}COOH$) and stearic acid ($C_{17}H_{35}COOH$) were first obtained from fats. The general formula of the homologous series is $C_nH_{2n+1}COOH$ or RCOOH whereas the functional group is the carboxyl group, —COOH. As only the hydrogen atom of the carboxyl group is replaceable by a metal, the fatty acids are all monobasic acids.

3. **Nomenclature of Fatty Acids.**—The fatty acids are commonly known by **trivial names** derived from the source of individual acids. For example, formic acid was so named because it was

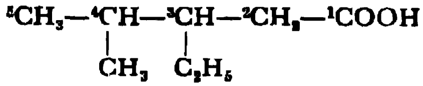
first obtained by distillation of ants (Latin : *formica*=ant). Similarly, the name acetic acid is derived from the Latin word, *acetum* for vinegar, of which it is the chief constituent. Their **IUPAC names** are derived from the names of the corresponding alkanes by replacing the final *e* with *oic* and adding the word *acid* as shown below :

Formula	*Common name*	*IUPAC name*
$HCOOH$	Formic acid	Methanoic acid
CH_3COOH	Acetic acid	Ethanoic acid
C_2H_5COOH	Propionic acid	Propanoic acid
C_3H_7COOH	Butyric acid	Butanoic acid
C_4H_9COOH	Valeric acid	Pentanoic acid
$C_5H_{11}COOH$	Caproic acid	Hexanoic acid
$C_6H_{13}COOH$	Heptoic acid	Heptanoic acid
$C_{15}H_{31}COOH$	Palmitic acid	Pentadecanoic acid
$C_{17}H_{35}COOH$	Stearic acid	Heptadecanoic acid

Sometimes acids are named as alkyl derivatives of acetic acid For example,

$CH_3CH_2CH_2COOH$ Ethylacetic acid $(CH_3)_2CH.COOH$ Dimethylacetic acid

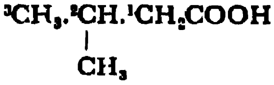
Complicated members are always named according to the IUPAC system and the substituents are indicated by numbers. Here the carboxyl group is always given number 1. For example,



$$^{5}CH_3-{}^{4}\underset{\displaystyle CH_3}{\underset{|}{C}H}-{}^{3}\underset{\displaystyle C_2H_5}{\underset{|}{C}H}-{}^{2}CH_2-{}^{1}COOH$$

is 3-ethyl-4-methylpentanoic acid.

Alternatively, the carboxyl group is regarded as a substituent and is denoted by adding the suffix carboxylic acid to the alkane. For example,



$$^{3}CH_3.{}^{2}\underset{\displaystyle CH_3}{\underset{|}{C}H}.{}^{1}CH_2COOH$$

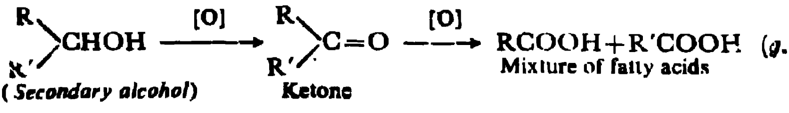
is 2-methylpropane-1-carboxylic acid or 3-methylbutanoic acid.

4. General Methods of Preparation of Fatty Acids.—

(*i*) *By the oxidation of alcohols, aldehydes or ketones with dichromate solution.*

$$CH_3CH_2OH \xrightarrow{[O]} CH_3CHO \xrightarrow{[O]} CH_3COOH \quad (g.\text{-}v.g.)$$

Ethyl alcohol (*Primary alcohol*) Acetaldehyde Acetic acid

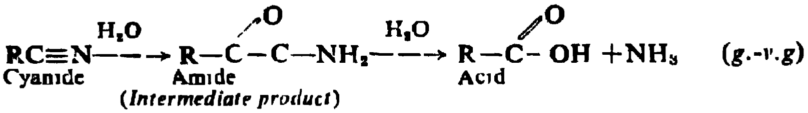


$$\begin{matrix}R\\R'\end{matrix}\!\!>CHOH \xrightarrow{[O]} \begin{matrix}R\\R'\end{matrix}\!\!>C=O \xrightarrow{[O]} RCOOH+R'COOH \quad (g.)$$

(*Secondary alcohol*) Ketone Mixture of fatty acids

In some cases an ester is obtained in place of the acid. Part of the alcohol is oxidised to the acid which forms an ester with the remaining alcohol.

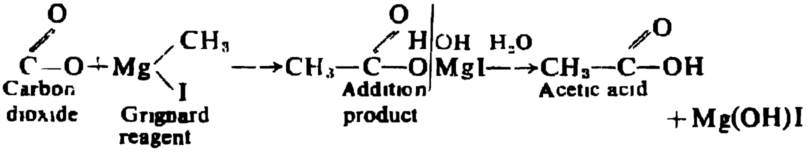
(*ii*) *By the hydrolysis of cyanides with acid or alkali.* This constitutes a very good synthetic method as cyanides can be easily obtained from alkyl halides.



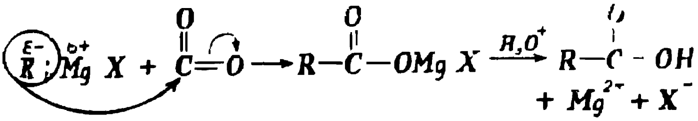
$$RC\equiv N \xrightarrow{H_2O} R-C-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{H_2O} R-\overset{O}{\overset{\|}{C}}-OH + NH_3 \quad (g.\text{-}v.g)$$

(*iii*) Higher fatty acids are commonly obtained *by the hydrolysis of natural fats*. For example, stearic acid is obtained from tristearin—a glyceride of stearic acid (*see* page 2 157).

(*iv*) *By the reaction between Grignard reagent and carbon dioxide e.g.*,

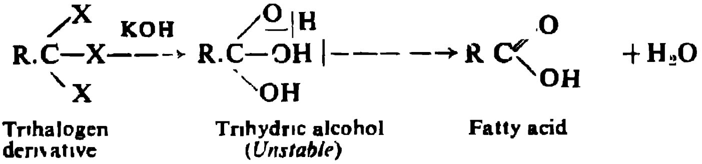


Mechanism of the reaction involved is given below :

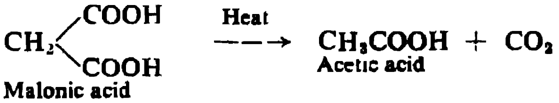


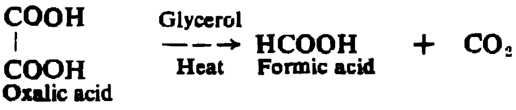
Addition product

(*v*) *By the hydrolysis of trihalogen derivatives in which the three halogen atoms are all attached to the same carbon atom.* The method is, however, of little practical importance, since all trihalogen derivatives, excepting those of methane, are inaccessible.



(*vi*) *By heating a dicarboxylic acid having two—COOH groups attached to the same carbon atom.* A molecule of carbon dioxide is eliminated and a monocarboxylic acid is obtained.



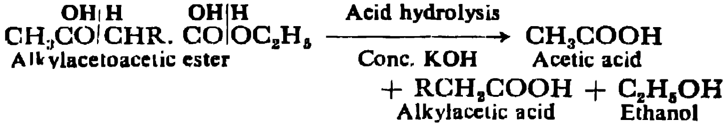


$$\underset{COOH}{\overset{COOH}{|}} \xrightarrow[\text{Heat}]{\text{Glycerol}} HCOOH + CO_2$$

(*vii*) ***By heating sodium alkoxide with carbon monoxide under pressure.*** Sodium salt of the fatty acid obtained may be hydrolysed with dilute mineral acid.

$$\underset{\text{Sod. alkoxide}}{RONa} + CO \longrightarrow \underset{\text{Sod. salt of acid}}{RCOONa} \xrightarrow{HCl} \underset{\text{Fatty acid}}{RCOOH}$$

(*viii*) ***From Malonic or Acetoacetic ester.*** Many fatty acids are conveniently synthesised from malonic or acetoacetic ester. For example,



$$\underset{\text{Alkylacetoacetic ester}}{CH_3CO\overset{OH\,|\,H}{|}CHR.\,CO\overset{OH\,|\,H}{|}OC_2H_5} \xrightarrow[\text{Conc. KOH}]{\text{Acid hydrolysis}} \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Alkylacetic acid}}{RCH_2COOH} + \underset{\text{Ethanol}}{C_2H_5OH}$$

These methods will be discussed in detail later.

(*ix*) A recent method for the preparation of higher fatty acids *is by the catalytic oxidation of long chain hydrocarbons.*

$$\underset{\text{Higher alkane}}{RCH_3} + \underset{\text{from air}}{2O_2} \xrightarrow[\text{stearate}]{\text{Manganese}} \underset{\text{Higher fatty acid}}{RCOOH} + H_2O$$

(*x*) Another recent method for the manufacture of fatty acids is by heating a mixture of an olefin, carbon monoxide and steam at 570-670K under pressure in the presence of phosphoric acid (catalyst).

$$CH_2{=}CH_2 + CO + H_2O \longrightarrow CH_3CH_2COOH$$

5. General Properties of Fatty Acids.—

(*a*) **Physical.** (*i*) The first three members are colourless, pungent-smelling, corrosive liquids. The acids from $C_4H_8O_2$ to $C_9H_{18}O_2$ are oily liquids smelling like goat's butter and the higher ones are odourless solids.

(*ii*) The specific gravity declines gradually from 1·22 for formic acid to 0·845 for stearic acid. Only the first two members are heavier than water.

(*iii*) The first four members are very soluble in water and the solubility decreases gradually with the rise of molecular weight (*cf.* alcohols). *This solubility is due to the acids being capable of forming hydrogen bonds with water.* All fatty acids dissolve readily in alcohol or ether.

(*iv*) The melting points of the normal fatty acids show alternation effect. The melting point of an even acid is always higher than that of the two odd acids immediately below and above it.

The boiling points, however, have a regular gradation.

(*v*) The lower members are far less volatile than is expected from their molecular weight. This is due to their being associated as a result of hydrogen bonding.

(*vi*) Their *acidity* decreases as the molecular weight increases ; the faint acidic character, however, persists among the higher homologues and they give salts and esters.

(b) **Chemical.** The molecule of a fatty acid (RCOOH) is made up of *(i)* an *alkyl group, R, and (ii)* the carboxyl group (—COOH). The properties of fatty acids are, therefore, the properties of these groups as given below :

(1) THOSE OF THE ALKYL GROUP

(i) **Halogenation.** Fatty acids may be readily halogenated in the *α-position*, *i.e.*, the hydrogen attached to the carbon adjacent to the carboxyl group is readily displaced. The reaction is best carried out in diffused sunlight or in the presence of halogen carrier (iodine, red phosphorus).

$$R.CH_2COOH \xrightarrow{P+Br_2} R.CHBr.COOH \xrightarrow{P+Br_2} R.CBr_2COOH$$

Similarly in acetic acid the three hydrogen atoms are successively replaced by halogen atoms (chlorine or bromine).

$$CH_3COOH + Cl_2 \rightarrow \underset{\text{Monochloroacetic acid}}{CH_2ClCOOH} + HCl$$

$$CH_2ClCOOH + Cl_2 \rightarrow \underset{\text{Dichloroacetic acid}}{CHCl_2COOH} + HCl$$

$$CHCl_2COOH + Cl_2 \rightarrow \underset{\text{Trichloroacetic acid}}{CCl_3COOH} + HCl$$

(ii) **Oxidation.** When acids are treated with mild oxidising agents (*e.g.*, hydrogen peroxide), the alkyl group is oxidised at the β-position. For example, butyric acid gives β-hydroxybutyric acid

$$\underset{\text{Butyric acid}}{CH_3.CH_2.CH_2.COOH} \xrightarrow{[O]} \underset{\text{β-hydroxybutyric acid}}{CH_3.CHOH.CH_2.COOH}$$

(2) THOSE OF THE CARBOXYL GROUP

(a) **Due to Replaceable Hydrogen Atom.** The fatty acids ionize in polar media to give hydrogen ions (H⁺) responsible for their acidic nature.

$$RCOOH \rightleftharpoons RCOO^- + H^+$$
$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

(i) **With alkalis and carbonates.** These are acidic towards litmus, neutralize alkalis forming salts and decompose carbonates and bicarbonates with effervescence when carbon dioxide gas is evolved.

$$RCOOH + NaOH \rightarrow RCOONa + H_2O$$
$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$
$$2CH_3COOH + Na_2CO_3 \rightarrow \underset{\text{Sod. acetate}}{2CH_3COONa} + H_2O + CO_2$$

(ii) **With metals.** With strongly electropositive metals like sodium and zinc, the fatty acids give salts with the liberation of hydrogen.

$$2RCOOH + Zn \rightarrow (RCOO)_2Zn + H_2$$
$$2CH_3COOH + 2Na \rightarrow \underset{\text{Sod. acetate}}{2CH_3COONa} + H_2$$

(b) Those involving the Hydroxyl Group

(i) **With alcohols.** Fatty acids react with alcohols in the presence of dehydrating agents like anhydrous zinc chloride or concentrated sulphuric acid, to form *esters*. (*Esterification*)

$$\underset{\text{Acetic acid}}{CH_3CO}\boxed{OH \quad + \quad H}\underset{\text{Ethyl alcohol}}{OC_2H_5} \rightleftharpoons \underset{\substack{\text{Ethyl acetate}\\ (Ester)}}{CH_3COOC_2H_5} \quad + \quad H_2O$$

(*For mechanism of Esterification of acids, see page 2·281.*)

(ii) **With Phosphorus halides or Thionyl chloride.** Phosphorus trichloride, phosphorus pentachloride and thionyl chloride react with fatty acids to give *acid chlorides*.

$$\underset{\text{Acid}}{3RCOOH} \quad + \quad PCl_3 \rightarrow \underset{\text{Acid chloride}}{3RCOCl} \quad + \quad H_3PO_3$$

$$\underset{\substack{\text{Acetic}\\ \text{acid}}}{CH_3COOH} \quad + \quad \underset{\substack{\text{Phosphorus}\\ \text{pentachoride}}}{PCl_5} \rightarrow \underset{\substack{\text{Acetyl}\\ \text{chloride}}}{CH_3COCl} \quad + \quad POCl_3 + HCl$$

$$\underset{\substack{\text{Propionic}\\ \text{acid}}}{C_2H_5COOH} + \underset{\substack{\text{Thionyl}\\ \text{chloride}}}{SOCl_2} \rightarrow \underset{\substack{\text{Propionyl}\\ \text{chloride}}}{C_2H_5COCl} \quad + \quad HCl \quad + \quad SO_2$$

(iii) **Dehydration.** Acetic anhydride is obtained by passing acetic acid vapours over a heated catalyst ($NaNH_4HPO_4+BPO_4$) at 875-895K.

$$2CH_3COOH \xrightarrow{-H_2O} (CH_3CO)_2O$$

Anhydrides of higher acids may be prepared by heating with acetic anhydride.

$$2RCOOH + \underset{\substack{\text{Acetic}\\ \text{anhydride}}}{(CH_3CO)_2O} \rightleftharpoons \underset{\substack{\text{Acid}\\ \text{anhydride}}}{(RCO)_2O} + 2CH_3COOH$$

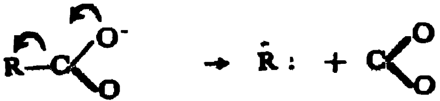
(c) Those involving Carboxyl Group as a whole

(i) *Dry distillation of the anhydrous alkali salts* of fatty acids with soda-lime yields *paraffins*.

$$R\boxed{COONa + NaO}H \rightarrow RH + Na_2CO_3$$

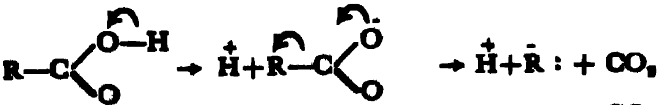
$$\underset{\text{Sod. acetate}}{CH_3\boxed{COONa + NaO}H} \rightarrow \underset{\text{Methane}}{CH_4} + Na_2CO_3$$

The mechanism of this decarboxylation is uncertain but it is believed that salts decompose by S_E1 reaction.



$$R: \quad +H^+ \rightarrow R—H$$

The decarboxylation of free acid is represented as follows :



$$\rightarrow R—H \quad + CO_2$$

Decarboxylation is favoured by presence of an electron-withdrawing group.

(*ii*) *Electrolysis of the concentrated aqueous solution of alkali salts of fatty acid gives paraffins* (*Kolbe's Reaction*). *For example*

At anode : $2CH_3COO^- \longrightarrow \underset{\text{Ethane}}{CH_3.CH_3} + 2CO_2 + 2e^-$

At cathode : $2H_2O + 2e^- \longrightarrow 2OH^- + H_2$

(*iii*) *Strong heating of the ammonium salt* of the fatty acids results in the formation of *acid amides* by the elimination of water.

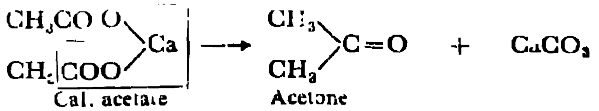
$$\underset{\text{Ammonium salt}}{RCOONH_4} \;—\; \underset{\text{Acid amide}}{RCONH_2} + H_2O$$

$$\underset{\text{Ammonium acetate}}{CH_3COONH_4} \;—\; \underset{\text{Acetamide}}{CH_3CONH_2} + H_2O$$

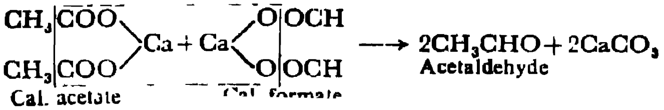
(*iv*) *Dehydration of ammonium salts* with phosphorus pentoxide results in the formation of a *cyanide*.

$$\underset{\text{Amm. acetate}}{CH_3COONH_4} \xrightarrow{P_4O_{10}} \underset{\text{Methyl cyanide}}{CH_3C\equiv N} + 2H_2O$$

(*v*) *Calcium salt* of a fatty acid other than formic acid, *when heated strongly, gives a ketone.* If, however, the *calcium salt is heated with calcium formate*, an *aldehyde* is obtained.



$$\underset{\text{Cal. acetate}}{(CH_3COO)_2Ca} \longrightarrow \underset{\text{Acetone}}{(CH_3)_2C=O} + CaCO_3$$



$$\underset{\text{Cal. acetate}}{(CH_3COO)_2Ca} + \underset{\text{Cal. formate}}{Ca(OOCH)_2} \longrightarrow \underset{\text{Acetaldehyde}}{2CH_3CHO} + 2CaCO_3$$

(*vi*) When silver salt of the fatty acid is heated with a halogen, it gives an alkyl halide. With an alkyl halide it gives an ester.

$$\underset{\substack{\text{Silver salt of}\\ \text{the fatty acid}}}{RCOO\,Ag} + X_2 \xrightarrow{\text{Heat}} \underset{\substack{\text{Alkyl}\\ \text{halide}}}{R{-}X} + CO_2 + AgX$$

$$RCOO\,Ag + XR' \longrightarrow \underset{\text{Ester}}{RCOOR'} + AgX$$

(*vii*) *Reduction.* All fatty acids are very resistant to reduction but prolonged heating of the fatty acid under pressure with concentrated hydriodic acid and small amount of red phosphorus results in its reduction to a *paraffin.* Reduction may also be effected by heating with hydrogen at high temperature and under pressure in the presence of a nickel catalyst.

$$\underset{\text{Fatty acid}}{RCOOH + 3H_2} \xrightarrow{Ni} \underset{\text{Paraffin}}{R.CH_3 + 2H_2O}$$

These can be easily reduced to corresponding alcohols with $LiAlH_4$. Primary alcohols are also produced by hydrogenation in presence of ruthenium or copper-chromium oxide catalyst.

$$RCOOH \xrightarrow{LiAlH_4} RCH_2OH$$

(*viii*) *Oxidation.* All the fatty acids, except formic acid, are extremely resistant to oxidation. These are, however, oxidised to carbon dioxide and water on prolonged heating with strong oxidising agents.

Mild oxidising agents oxidise them to β-hydroxy acids (*see* page 2·224).

6. Detection of the Carboxyl Group.—The presence of a carboxyl group in an organic compound is confirmed by the following tests :

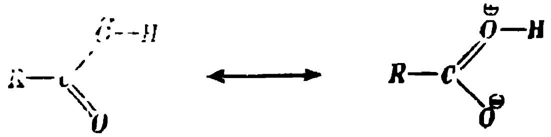
(*i*) If the organic compound is soluble in water and is acidic towards litmus, treat it with sodium bicarbonate solution. Evolution of carbon dioxide with brisk effervescence shows the presence of a carboxyl group provided sulphur is absent as shown by elementary quantitative analysis.

(*ii*) If the compound is insoluble in water but dissolves in sodium bicarbonate solution with the evolution of carbon dioxide, it is a carboxylic acid.

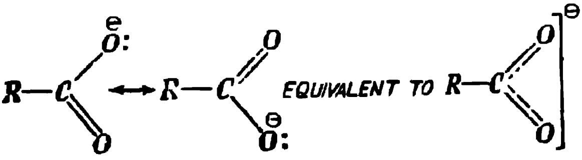
Other acidic substances like sulphonic acid and phenol are absent because the elementary qualitative analysis has shown the absence of sulphur (implies absence of sulphonic acid) and the substance decomposes a bicarbonate solution (phenol does not react with it).

7. **Structure of Carboxylic Group.** The carboxylic acid as well as the carboxylate ion are considered to be resonance hybrids as shown below :

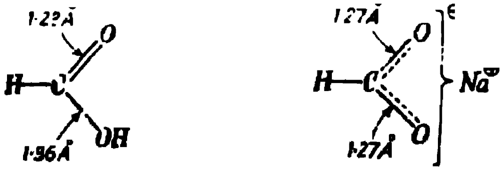
(*a*) *Carboxylic acid* :



(*b*) *Carboxylate ion* :

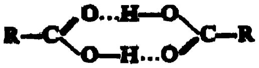


The negative charge is evenly distributed over both oxygen atoms. This is supported by the evidence of bond lengths in carboxylic acid and carboxylate ion. For example, in formic acid and formate ion,



Formic acid Sod. formate

Carboxylic acids are highly associated in the liquid state but in the vapour phase they tend to form dimers. The two molecules are linked through hydrogen bonding shown by dotted lines as given below :

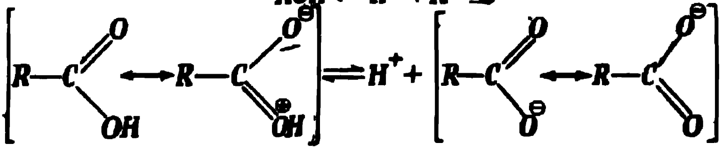


C=O group in an acid is rather inert. Due to resonance of acid molecule, C=O will have some single-bond character and C—OH bond will have some double-bond character. The length of C=O bond is, therefore, greater than that of a pure C=O bond. Similarly C—OH bond is shorter than pure C—OH bond. That is why the C=O group in an acid is rather inert.

8. Acidity of Carboxylic Acids.—Strength of an acid or its acidity is proportional to the relative ease with which it loses a proton leaving behind the anion. *It is determined chiefly by the difference in stability between the acid and its anion.* Both alcohol and acid release proton but the latter does it much more readily. Let us account for this fact.

Alcohol and the alkoxide ion are each represented by a single structure. The carboxylic acid and the carboxylate ion are each represented by two resonance structures and are, therefore, resonance hybrids.

$$ROH \rightleftharpoons H^{\oplus} + R—O^{\ominus}$$



I II III IV

Carboxylic acid
Resonance hybrid of
non-equivalent structures.

Carboxylate ion
Resonance hybrid of
equivalent structures.

Although both acid and carboxylate anion are stabilised by resonance, stabilization is far greater for the anion than for the acid. This is due to two equivalent resonance structures contributing to the carboxylate anion. The acidity of a carboxylic acid is thus due to the powerful resonance stabilization of its anion. *This stabilization and resulting acidity are possible only because of the presence of carboxyl group.*

Alkoxide anion from alcohol does not show resonance and is not stabilized. This lack of stabilization is responsible for a very weak acidity of alcohols.

$$R—O—H \rightleftharpoons R—\bar{O} + \overset{+}{H}$$

no resonance
hybrid

Order of Acid strengths :

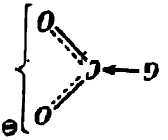
$RCOOH > HOH > ROH > CH \equiv CH > NH_3 > RH$

Order of Basic strengths :

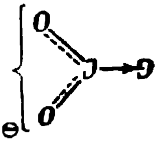
$RCO\bar{O} < \bar{O}H < R\bar{O} < CH \equiv \bar{C} < \bar{N}H_2 < R^-$

Effect of Substituents on Acidity. Any factor that stabilizes the anion more than it stabilizes the acid should increase the acidity and any factor that makes the anion less stable should decrease acidity.

An electron-withdrawing substituent stabilizes the anion by dispersing the negative charge and, therefore, increases the acidity. On the other hand, electron-releasing substituents intensify the negative charge on the anion resulting in decrease of stability and thus decrease the acidity of the acid.



An electron-withdrawing substituent G withdraws electrons and stabilizes the anion (*Acidity increases*)



An electron-releasing substituent G releases electrons and destabilizes the anion (*Acidity decreases*)

For example, electron-releasing alkyl groups weaken acids, while electron-withdrawing halogens strengthen the acids. Thus CH_3COOH (acetic acid) is about one-tenth as strong as $HCOOH$, and C_2H_5COOH (propionic acid) containing a larger alkyl group is weaker still. Chloro-acetic acid ($CH_2Cl.COOH$) is 100 times as strong as acetic acid, $CHCl_2.COOH$ is still stronger and $CCl_3.COOH$ is 10,000 times as strong as CH_3COOH.

Electron-withdrawing nature of various halogens is in the order :

$$F > Cl > Br > I$$

Hence, strength of halogen-substituted acids is in the order :

$$FCH_2COOH > ClCH_2COOH > BrCH_2\ CHOO > ICH_2COOH$$

$CH_3CHCl.COOH$ is stronger than $CH_2ClCH_2.COOH$ since inductive effect of chlorine in α-position is stronger than in β-position.

Measure of Acidity of Acids. The carboxylic acid RCOOH ionizes as follows :

$$RCOOH + H_2O \rightleftharpoons RCO\bar{O} + H_3\overset{+}{O}$$

The equilibrium constant for the system is termed ionization constant, K_a of the acid and is a measure of the acidity of the acid.

$$K_a = \frac{[RCOO^-][H_3\overset{+}{O}]}{[RCOOH]}$$

Water being present in large excess, $[H_2O]$ remains constant and is omitted. K_a values of some acids are given below. These will help us to know the relative acidity of various acids. The values given below confirm the order of acidity of various acids and substituted acids.

Table 23·1—K_a values of Some acids at 398 K

Acid	K_a	*Acid*	K_a
HCOOH	$17{\cdot}7\times10^{-5}$	CH_2FCOOH	260×10^{-5}
CH_3COOH	$1{\cdot}75\times10^{-5}$	$CH_2ClCOOH$	136×10^{-5}
C_2H_5COOH	$1{\cdot}3\times10^{-5}$	$CH_2BrCOOH$	125×10^{-5}
C_6H_5COOH	$6{\cdot}3\times10^{-5}$	CH_2ICOOH	67×10^{-5}
$CH_3.C_6H_4COOH$	$4{\cdot}2\times10^{-5}$	$CHCl_2COOH$	$5{\cdot}5\times10^{-2}$
		CCl_3COOH	$23{\cdot}2\times10^{-2}$

INDIVIDUAL MEMBERS

9. **Formic Acid, Methanoic Acid, HCOOH.**—The first member of the acid series is formic acid. It occurs in red ants (whence the name), in the stings of bees and wasps and also in the bristles of stinging nettles (बिच्छू बूटी).

Preparation. Formic acid may be prepared by any of the general methods used for the preparation of fatty acids. It is, however, **prepared industrially** *by heating sodium hydroxide with carbon monoxide at 483K and under 6-10 atmosphere pressure.*

$$NaOH + CO \rightarrow HCOONa$$

The sodium formate is distilled with dilute sulphuric acid when an aqueous solution of formic acid is obtained.

$$2HCOONa + H_2SO_4 \rightarrow 2HCOOH + Na_2SO_4$$

To prepare the anhydrous acid, the sodium salt is warmed with a mixture of concentrated sulphuric acid and anhydrous formic acid. In the presence of the latter, concentrated sulphuric acid has very little tendency to dehydrate formic acid.

Formic acid may be **prepared in the laboratory** (*i*) *by passing methyl alcohol vapour, or formaldehyde mixed with air over platinum black (catalyst).*

$$\underset{\text{Methanol}}{CH_3OH} + O_2 \xrightarrow{\text{Platinum black}} \underset{\text{Formic acid}}{HCOOH} + H_2O$$

$$\underset{\text{Formaldehyde}}{2HCHO} + O_2 \longrightarrow \underset{\text{Formic acid}}{2HCOOH}$$

(*ii*) Formic acid is more conveniently prepared in the laboratory by heating glycerol with oxalic acid at 370-380K in a distillation flask fitted with a thermometer and a condenser (Fig. 23·1). Glyceryl monoxalate first produced loses carbon dioxide to give glyceryl monoformate (monoformin).

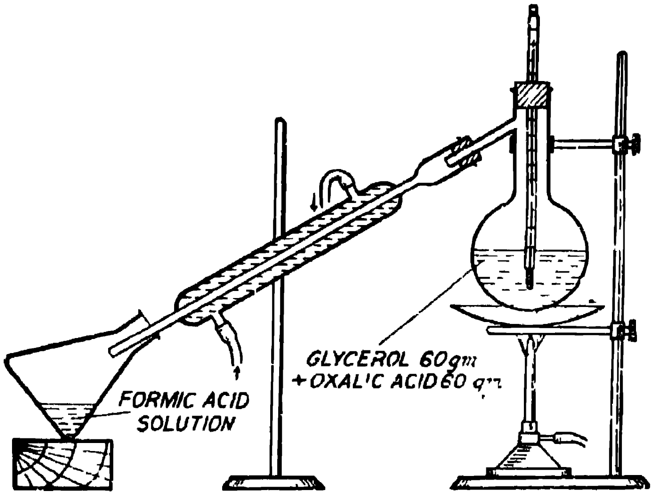
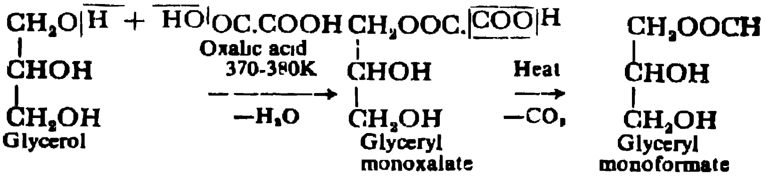
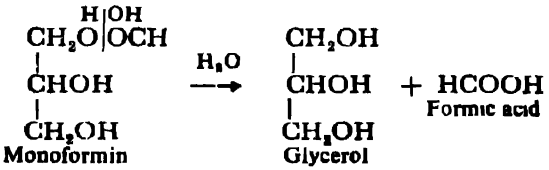


Fig. 23 1—Preparation of formic acid in the laboratory.



$$\underset{\text{Glycerol}}{\begin{array}{l} CH_2O|H \\ | \\ CHOH \\ | \\ CH_2OH \end{array}} + HO|OC.COOH \xrightarrow[-H_2O]{\text{Oxalic acid } 370\text{-}380K} \underset{\text{Glyceryl monoxalate}}{\begin{array}{l} CH_2OOC.|COO|H \\ | \\ CHOH \\ | \\ CH_2OH \end{array}} \xrightarrow[-CO_2]{\text{Heat}} \underset{\text{Glyceryl monoformate}}{\begin{array}{l} CH_2OOCH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}}$$

When the evolution of carbon dioxide decreases, more oxalic acid is added. The monoformin is now hydrolysed to glycerol and formic acid.



$$\underset{\text{Monoformin}}{\begin{array}{l} \quad\; H|OH \\ CH_2O|OCH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}} \xrightarrow{H_2O} \underset{\text{Glycerol}}{\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}} + \underset{\text{Formic acid}}{HCOOH}$$

An aqueous solution of formic acid distils over, and the regenerated glycerol reacts with fresh oxalic acid added. Thus the cycle of changes is repeated and small quantity of glycerol can convert a large amount of oxalic acid into formic acid.

PREPARATION OF ANHYDROUS FORMIC ACID. The aqueous solution of formic acid obtained above cannot be fractionated to get anhydrous acid because the boiling point of the acid is 373·5K. The aqueous solution is neutralized with litharge or lead carbonate and concentrated to get lead formate crystals. The crystals are dried and heated at 373K in a current of hydrogen sulphide when the anhydrous formic acid distils over.

$$\underset{\text{Lead formate}}{(HCOO)_2Pb} + H_2S \rightarrow \underset{\text{Formic acid}}{2HCOOH} + PbS$$

The anhydrous acid is contaminated with a small quantity of hydrogen sulphide. To free it from the latter it is redistilled over some dry lead formate.

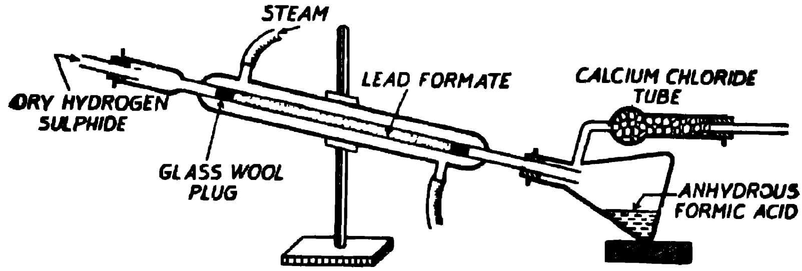
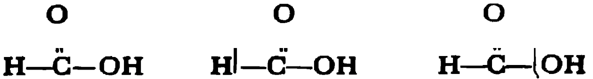


Fig. 23·2—Preparation of anhydrous formic acid.

10. Properties of Formic Acid.

(*a*) **Physical.** Formic acid is a colourless, pungent-smelling mobile liquid (m.p.=281·4K ; b.p.=373·5K). It is miscible in all proportions with water, alcohol and ether. It is corrosive and produces blisters on the skin.

(*b*) **Chemical.** Formic acid behaves both as an acid and as an aldehyde. The dual behaviour is justified by its structural formula wherein both carboxyl and the aldehyde groups are present as indicated below :

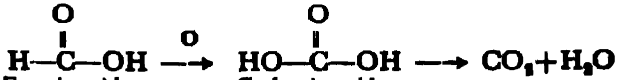


$$H-\overset{\overset{\displaystyle O}{\|}}{C}-OH \qquad H|-\overset{\overset{\displaystyle O}{\|}}{C}-OH \qquad H-\overset{\overset{\displaystyle O}{\|}}{C}-|OH$$

Formic acid Carboxyl group Aldehyde group

(1) ACIDIC NATURE. Formic acid gives the general reactions of the fatty acids. It is a stronger acid than any of its homologues and is about twelve times as strong as acetic acid. Thus it turns blue litmus red, neutralizes alkalis, decomposes carbonates and dissolves certain metallic oxides. Formates obtained are all soluble in water except those of silver and lead which are sparingly soluble.

(2) REDUCING ACTION. Formic acid and formates are strong reducing agents like the aldehydes. It reduces ammoniacal silver nitrate, acidified potassium permanganate, and the salts of many heavy metals, *e.g.*, it reduces mercuric chloride to mercurous chloride or mercury. During these reductions, formic acid is oxidised to carbonic acid.



$$\underset{\text{Formic acid}}{H-\overset{\overset{\displaystyle O}{\|}}{C}-OH} \xrightarrow{O} \underset{\text{Carbonic acid}}{HO-\overset{\overset{\displaystyle O}{\|}}{C}-OH} \longrightarrow CO_2+H_2O$$

(*a*) An acidified solution of potassium permanganate is decolorised due to reduction.

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O] \times 2$$
$$HCOOH \rightarrow CO_2 + 2H^+ + 2e^-] \times 5$$
$$\overline{2MnO_4^- + 6H^+ + 5HCOOH \rightarrow 2Mn^{2+} + 8H_2O + 5CO_2}$$

(*b*) Ammoniacal silver nitrate is reduced to silver mirror (metallic silver).

$$2Ag(NH_3)_2^+ + HCOOH \rightarrow 2Ag + CO_2 + 2NH_4^+ + 2NH_3$$

(3) DEHYDRATION. With concentrated sulphuric acid, formic acid is dehydrated to carbon monoxide and water.

$$HCOOH \xrightarrow{H_2SO_4} CO + H_2O$$

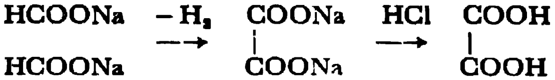
This reaction is used for the preparation of carbon monoxide in the laboratory.

(4) DECOMPOSITION. When heated under pressure at 433K, formic acid decomposes to give carbon dioxide and hydrogen.

$$HCOOH \rightarrow CO_2 + H_2$$

(5) ACTION OF HEAT ON FORMATES.

(*i*) Sodium or potassium formate when heated rapidly to 633K, loses hydrogen and gives the oxalate. The reaction has been used for the manufacture of oxalic acid which can be liberated by treating the sodium salt with dilute hydrochloric acid.



$$\begin{array}{l}\text{HCOONa}\\ \text{HCOONa}\end{array} \xrightarrow{-H_2} \begin{array}{l}\text{COONa}\\ |\\ \text{COONa}\end{array} \xrightarrow{HCl} \begin{array}{l}\text{COOH}\\ |\\ \text{COOH}\end{array}$$

Sod. formate (*Two molecules*) Sodium oxalate Oxalic acid

(*ii*) On heating the alkali formate with soda-lime, hydrogen is evolved.

$$H|\overline{\underline{COONa + NaO}}|H \longrightarrow H_2 + Na_2CO_3$$

(*iii*) Ammonium formate on heating gives formamide.

$$\underset{\text{Amm. formate}}{HCOONH_4} \longrightarrow \underset{\text{Formamide}}{HCONH_2} + H_2O$$

(*iv*) Calcium formate on heating gives formaldehyde (*cf.* other calcium salts which produce ketones).

$$\underset{\text{Calcium formate}}{(HCOO)_2Ca} \longrightarrow \underset{\text{Formaldehyde}}{HCHO} + CaCO_3$$

11. Uses.—Formic acid is used :

(*i*) As an antiseptic and for preservation of fruit.

(*ii*) In tanning for removing lime from the leather.

(*iii*) In dyeing wool and cotton fabrics.

(*iv*) In coagulating rubber.

(*v*) Nickel formate is used as a catalyst in hydrogenation of oils.

12. Tests for Formic Acid and Formates.—

(*i*) Neutral solutions of formates give a red colour with ferric chloride solution (*neutral*). Formic acid is neutralised with ammonia before testing.

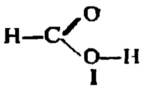
(*ii*) With ammoniacal silver nitrate solution they give silver mirror.

(*iii*) With mercuric chloride these produce a white precipitate of mercurous chloride.

(*iv*) On heating with concentrated sulphuric acid, carbon monoxide is liberated, which burns with a blue flame.

13. **Structure of Formic Acid.**—(*i*) Molecular formula of formic acid as determined from its analytical data and molecular weight determination is CH_2O_2.

(*ii*) Assuming that carbon is tetravalent, oxygen bivalent and hydrogen monovalent, two possible structures of formic acid are :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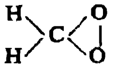
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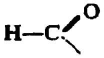
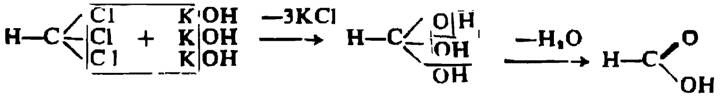
(*iii*) Formic acid is monobasic and only one hydrogen atom is replaceable by a metal. This suggests that the two hydrogen atoms are in a different state of combination as in formula I.

(*iv*) Formic acid is a strong reducing agent like aldehydes. This suggests the existence of aldehyde group,  as in formula I.

(*v*) The formula I for formic acid is further confirmed by its formation from chloroform and caustic potash.



14. **Acetic Acid, Ethanoic Acid, CH_3COOH.**—In the form of vinegar, acetic acid has been known since very early times. It is found free in a number of fruit juices and in combined state in many oils and essential oils. It is one of the commonest organic acids.

15. **Preparation.**—Acetic acid can be prepared by any of the general methods of preparation of fatty acid given before. It is, however, prepared industrially as follows :

(1) **From Acetylene.** The modern method for the manufacture of acetic acid is from acetylene obtained from calcium carbide. Acetylene is passed through 42% sulphuric acid at 333K containing 1% mercuric sulphate to get acetaldehyde. This is further oxidised to acetic acid by passing a mixture of air and acetaldehyde vapours at about 343K under pressure over manganese acetate (*catalyst*).

$$\underset{\text{Acetylene}}{CH{\equiv}CH+H_2O} \xrightarrow[HgSO_4]{H_2SO_4+} \underset{\text{Acetaldehyde}}{CH_3CH{=}O} \xrightarrow{O} \underset{\text{Acetic acid}}{CH_3COOH}$$

The yield is *very good* and the strength of the acid prepared is about 97 per cent. The method is quite cheap and about 75 per cent of acetic acid needed in the U.S.A. is manufactured by this method.

(2) **From Pyroligneous acid.** Pyroligneous acid is an aqueous liquor obtained when volatile products from wood distillation are passed through water. It contains acetic acid (9-10%), methyl alcohol (2-3%) and acetone (0·5%). It is boiled and the vapours are led through boiling milk of lime where acetic acid forms calcium acetate while the other constituents pass over.

The calcium acetate is dried and distilled with concentrated sulphuric acid when dilute acetic acid (70-75%) distils over. The dilute acid is neutralized with sodium hydroxide and evaporated to give sodium acetate. This is fused and distilled with concentrated sulphuric acid when *glacial* acid (100%) is obtained.

With the discovery of cheap synthetic method for the manufacture of acetic acid, this method has become obsolete.

(3) **Fermentation Process.** The manufacture of acetic acid by *fermentation process* is based upon the oxidation of fermented liquors (10-15% alcohol) by air under the influence of *mycoderma aceti*. A 3-7 per cent solution of the acid obtained is called **vinegar.**

$$C_2H_5OH+O_2 \longrightarrow CH_3COOH+H_2O$$

In the *Quick Vinegar Process*, wooden vats with perforated tops and false bottoms (Fig. 23·3) are packed with beachwood shavings moistened with old vinegar (*ferment*). Dilute alcohol solution (a 10 per cent aqueous solution of ethanol, containing phosphate and inorganic salts which are necessary for the fermentation) is then made to trickle down while a current of air is blown in. The dilute acid obtained is recirculated through this tower or other similar towers used in series till the concentration reaches 8-10 per cent. The following points should be carefully noted :

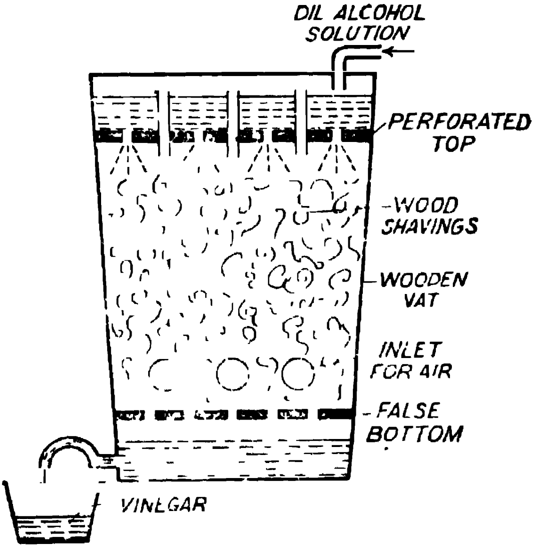


Fig. 23·3—Quick Vinegar Process.

(*i*) When the percentage of alcohol in the fermented liquor used is more than 15, the cell walls of the bacteria are hardened and they lose their activity. In pure dilute alcohol solution they do not grow because they have nothing like nitrogenous matter there for their maintenance.

(*ii*) The supply of air should be carefully regulated. With less air, oxidation proceeds only up to acetaldehyde while with too much of air oxidation proceeds still further to carbon dioxide and water.

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} \xrightarrow{O} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{O} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{O} 2CO_2+2H_2O$$

(*iii*) Flow of alcohol is to be regulated in order to maintain the temperature between 303-308K at which temperature fermentation proceeds best.

It is only recently that vinegar has been used as a source of commercial acetic acid. This is entirely due to the introduction of highly efficient methods of fractionation. Vinegar is fractionated to get glacial acetic acid.

16. **Properties** : (*a*) **Physical.**—At ordinary temperature, acetic acid is a colourless, corrosive liquid with a pungent smell of its own but below 290K it solidifies to an icy mass which gives it the name *glacial acetic acid*. It boils at 391K and its specific gravity is 1·08 at 273K. It is miscible with water, alcohol and ether in all proportions. Acetic acid is a good solvent for sulphur, phosphorus, iodine and many organic compounds.

(*b*) **Chemical.** Acetic acid is a typical member of fatty acids. Its reactions have already been discussed under general reactions of fatty acids.

17. **Uses.**—(*i*) Acetic acid is used in the manufacture of various dyestuffs, perfumes and rayons.

(*ii*) In the manufacture of rubber from latex and casein from milk, acetic acid is used for coagulation.

(*iii*) Its salts are used in medicine and also paints.

(*iv*) Acetates of aluminium and chromium are used as mordants.

(*v*) Dilute acid is used as vinegar for table purposes while concentrated acid is used as a solvent.

(*vi*) Its organic esters are generally used as perfumes.

18. **Tests for Acetates and Acetic Acid.**

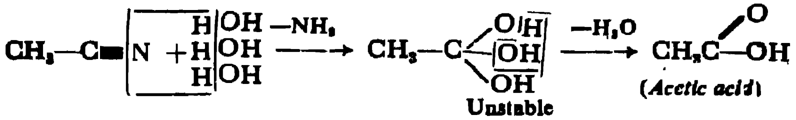
(*i*) *Heating with concentrated sulphuric acid.* When an acetate is heated with a few drops of concentrated sulphuric acid, a characteristic vinegar odour is perceived.

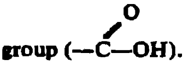
(*ii*) *Fruity odour test.* A banana smell due to the formation of ethyl acetate on heating with alcohol and concentrated sulphuric acid is confirmatory test for all acetates.

(*iii*) *Action of ferric chloride.* A drop of neutral ferric chloride in a neutral solution of acetate gives a red coloration which gives a reddish precipitate on heating.

19. Structure of Acetic acid.—(*a*) Molecular formula of acetic acid as calculated from its analytical data and molecular weight determination is $C_2H_4O_2$.

(*b*) From its preparation by the hydrolysis of methyl cyanide,



we conclude that its structure is as indicated above and contains one methyl group (CH_3—) and one hydroxyl group (—OH) which form part of the carboxyl group  $(—\overset{O}{\overset{\|}{C}}—OH)$.

(*c*) This view is supported by its reactions :

(*i*) On chlorination, three of its hydrogen atoms are replaced by chlorine atoms. These are hydrogen atoms of the methyl group.

(*ii*) With phosphorus pentachloride, one hydrogen atom along with one oxygen atom is replaced by one chlorine atom, showing the presence of one monovalent hydroxyl group.

(*iii*) With sodium only one of the hydrogen atoms is replaced, showing this hydrogen to be different from the remaining three. This is hydrogen atom of the hydroxyl (OH) group, different from the remaining hydrogen atoms which are present in the methyl (CH_3) group.

20. Comparison of Formic Acid and Acetic Acid.

—Both formic and acetic acids contain a carboxyl group. The points of similarity between the two acids as given below are, in fact, properties of the carboxyl group. Acetic acid contains a methyl group attached to the carboxyl group whereas formic acid has only a hydrogen atom in place of methyl group. The points of difference between them as given below are the reactions of methyl group and the lonely hydrogen atom which can be easily oxidised, thus rendering formic acid a strong reducing agent.

Points of Similarity : (*i*) Both give salts with alkalis and carbonates.

(*ii*) Both form esters (formates and acetates) when heated with an alcohol and sulphuric acid.

(*iii*) Both give acid chlorides with phosphorus pentachloride. Formyl chloride produced is unstable whereas acetyl chloride is stable.

(*iv*) Ammonium salts of both the acids give amides (formamide and acetamide) when heated.

Points of Difference : The points of difference between the two acids are given below in the table :

Formic acid	Acetic acid
1. Decomposes on heating to give carbon dioxide and hydrogen.	Stable.
2. With concentrated sulphuric acid, gives carbon monoxide and water.	Stable.
3. With halogens, there is no action.	Substituted acids are formed.
4. Reduces ammoniacal silver nitrate and Fehling's solution.	No action.
5. Calcium salt on heating gives formaldehyde.	Calcium salt on heating gives acetone.
6. Sodium salt on heating gives sodium oxalate+hydrogen.	No action.
7. Sodium salt+soda lime give hydrogen on heating.	Methane is produced.
8. Electrolysis of alkali salt solution gives hydrogen.	Ethane is obtained.

21. Vinegar (सिरका).—When the percentage of alcohol is less than 15 in a liquor, a living organism, *mycoderma aceti* which is always present in air, can bring about the **acetous fermentation**. It is an oxidation brought about by bacteria. It was Pasteur who studied this problem first—"Why wines go bad". Vinegar is only a dilute solution of acetic acid containing colouring matter and other substances like some other organic acids, their esters, sugar and dextrin which impart it the usual pleasant taste. Four to five per cent acetic acid to which burnt sugar is added to give it colour forms the common vinegar—only an imitation of vinegar, sold in bazar, is devoid of the usual pleasant taste of real vinegar.

Vinegar is manufactured by two different methods as described below :

(*i*) **Slow Vinegar Process or the Old French Process.** Several shallow wooden vats, moistened with a little vinegar to supply the ferment, are filled with light wine and exposed to air. After a few days alcohol present in wine is oxidised to vinegar which can be siphoned off and fresh charge added.

In India common method used for preparation of vinegar is by exposing sugarcane juice to air for a long time. A little of vinegar is sometimes added to supply the ferment which is otherwise supplied by air. Fermentation sets in and sugar gets converted into vinegar.

(*ii*) **Quick Vinegar Process or the German Process.** The vinegar obtained by the slow process is of better quality and is generally used for table purposes while one produced by quick process (*see* page 2·235) is put to industrial uses.

22. Propionic acid, *Propanoic acid*, **C_2H_5COOH**.—Propionic acid is prepared industrially by the oxidation of *n*-propyl alcohol.

$$\underset{\text{1-Propanol}}{CH_3.CH_2.CH_2OH} \xrightarrow{[O]} \underset{\text{Propionic acid}}{CH_3.CH_2.COOH}$$

It is a colourless, oily liquid (b.p. 414K) having an acid odour. It is miscible with water, ethanol and ether in all proportions.

23. Butyric acid, *Butanoic acid*, **C_3H_7COOH**.—Two isomeric butyric acids are known.

***n*-Butyric acid**, $CH_3.CH_2CH_2.COOH$, occurs free in perspiration, as the glyceryl ester in butter. It is prepared industrially :

(*i*) By the oxidation of *n*-butyl alcohol.

(*ii*) By the butyric fermentation of carbohydrates with the help of the micro-organism *Bacillus butyricus*.

It is a viscous liquid (b.p. 435K) smelling like rancid butter and is miscible with water, alcohol and ether.

Isobutyric acid, $(CH_3)_2CH.COOH$, occurs free and in the combined state as esters in many plants. It is prepared industrially by oxidation of isobutyl alcohol.

$$(CH_3)_2CH.CH_2OH \xrightarrow{[O]} (CH_3)_2CH.COOH$$

It may also be prepared synthetically as follows :

$$\underset{\text{Isopropyl alcohol}}{(CH_3)_2CHOH} \xrightarrow{P+I_2} \underset{\text{Isopropyl iodide}}{(CH_3)_2CHI} \xrightarrow{KCN} \underset{\text{Isopropyl cyanide}}{(CH_3)_2CHCN}$$

$$\xrightarrow{H_2O} \underset{\text{Isobutryric acid}}{(CH_3)_2CH.COOH}$$

It is a colourless, oily liquid (b.p. 427K), sparingly soluble in water. Its calcium salt is more soluble in hot water than in cold and thus differs from calcium salt of *n*-butyric acid which is more soluble in cold water than in hot.

Unlike the normal acid, it is more readily oxidised to acetone or acetic acid and carbon dioxide.

24. Higher Fatty Acids.

Palmitic acid (*hexadecoic acid*), $C_{15}H_{31}COOH$ occurs as glyceryl ester in palm oil. It is a colourless waxy solid (m.p. 337K).

Stearic acid (*octadecoic acid*), $C_{17}H_{35}COOH$ is prepared industrially by hydrolysis of tristearin, a solid fat and hence its name (Greek: *stear*= tallow). It is a colourless waxy solid (m.p. 345K) used in the manufacture of candles and face cream.

The sodium and potassium salts of palmitic and stearic acids are the constituents of ordinary soaps.

UNSATURATED MONOCARBOXYLIC ACIDS

25. Nomenclature.—Unsaturated acids are usually known by their common names. For naming these according to the IUPAC system, the longest carbon atoms chain with the carboxyl group and the double bond is selected. Their relative positions are indicated by numbers, *e.g.*, $^5CH_3.^4CH={}^3CH^2CH_2{}^1COOH$ is 3-pentenoic acid.

Alternatively, the unsaturated acid is named as the substitution product of an olefin, *e.g.*, the above acid will be named as but-2-ene-1-carboxylic acid. Some common members are :

Formula	*Common name*	*IUPAC name*
$CH_2{=}CH.COOH$	Acrylic acid	2-Propenoic acid
$CH_3.CH{=}CH.COOH$	Crotonic acid	2-Butenoic acid

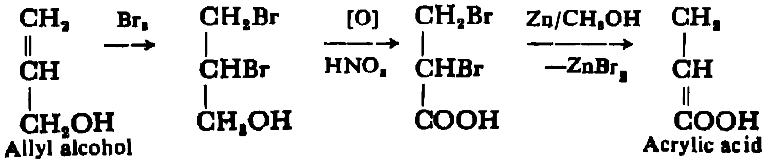
26. Acrylic Acid, 2-Propenoic Acid, $CH_2{=}CH.COOH$.

Preparation. Acrylic acid is prepared :

(*i*) *By the oxidation of acrolein with ammoniacal silver nitrate.*

$$\underset{\text{Acrolein}}{CH_2{=}CH.CHO} + [O] \xrightarrow[AgNO_3]{Amm.} \underset{\text{Acrylic acid}}{CH_2{=}CH.COOH}$$

(*ii*) *By oxidation of allyl alcohol after protecting the double bond as follows* :

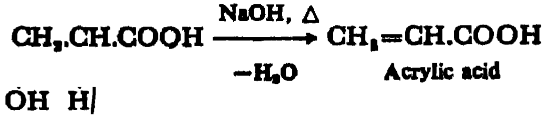


$$\underset{\text{Allyl alcohol}}{\begin{matrix}CH_2\\ \|\\ CH\\ |\\ CH_2OH\end{matrix}} \xrightarrow{Br_2} \begin{matrix}CH_2Br\\ |\\ CHBr\\ |\\ CH_2OH\end{matrix} \xrightarrow[HNO_3]{[O]} \begin{matrix}CH_2Br\\ |\\ CHBr\\ |\\ COOH\end{matrix} \xrightarrow[-ZnBr_2]{Zn/CH_3OH} \underset{\text{Acrylic acid}}{\begin{matrix}CH_2\\ |\\ CH\\ \|\\ COOH\end{matrix}}$$

(*iii*) *By heating α-bromopropionic acid with alcoholic potash.*

$$\underset{\text{α-bromopropionic acid}}{CH_3.CHBr.COOH} + \underset{(\textit{Alcoholic})}{KOH} \longrightarrow \underset{\text{Acrylic acid}}{CH_2{=}CH.COOH} + KBr + H_2O$$

(*iv*) *By heating β-hydroxypropionic acid with aqueous caustic soda or by heating ethylene cyanohydrin with sulphuric acid.*



$$\underset{\text{β-hydroxypropionic acid}}{\underline{CH_2.\overset{}{\underset{OH}{}}CH.\underset{H|}{}COOH}} \xrightarrow[-H_2O]{NaOH,\ \Delta} \underset{\text{Acrylic acid}}{CH_2{=}CH.COOH}$$

$$CH_2OH.CH_2CN \xrightarrow{H_2SO_4} \underset{\text{β-hydroxypropionic acid}}{CH_2OH.CH_2.COOH} \xrightarrow{-H_2O} CH_2{=}CH.COOH$$

(*v*) A new method for its manufacture *is by the interaction of acetylene, CO and water in presence of nickel (catalyst).*

$$CH{\equiv}CH + CO + H_2O \longrightarrow CH_2{=}CH.COOH$$

Properties. Acrylic acid is a colourless pungent-smelling liquid (b.p. 414K) miscible with water in all proportions.

Chemical properties of acrylic acid are the general properties of unsaturated acids. It behaves both as an acid and as an alkene as shown by its following reactions :

(*i*) *Reduction.* With nascent hydrogen it gives propionic acid

$$CH_2{=}CH.COOH + 2[H] \xrightarrow{Na/C_2H_5OH} CH_3.CH_2.COOH$$

(*ii*) *Addition of Halogens.* With halogens it gives addition products.

$$CH_2{=}CH.COOH + Br_2 \rightarrow \underset{\text{α, β-dibromopropionic acid}}{CH_2Br.CHBr.COOH}$$

(*iii*) *Addition of Halogen acids.* It gives β-halogenopropionic acid contrary to the Markownikoff's rule.

$$CH_2{=}CH.COOH + HCl \rightarrow \underset{\text{β-chloropropionic acid}}{CH_2Cl.CH_2.COOH}$$

. *During addition of halogen acids to αβ- and βγ-unsaturated acids the halogen atom attaches to the unsaturated carbon atom away from the carboxyl group.* This may be ascribed to the inductive effect of carboxyl group (*cf.*, allyl alcohol).

Addition of halogen acids to γδ-unsaturated acids takes place in accordance with Markownikoff's rule. This is explained by saying that the inductive effect of carboxyl group ceases beyond β-carbon atom.

$$\underset{\text{4-Pentenoic acid}}{CH_2{=}CH.CH_2.CH_2.COOH} + HBr \longrightarrow \underset{\text{γ-bromovaleric acid}}{CH_3CHBr.\_\_\_\_\_\_}$$

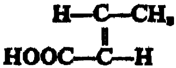
(*iv*) *Oxidation.* With dilute potassium permanganate acrylic acid is oxidised to glyceric acid whereas oxalic acid is produced on vigorous oxidation.

$$CH_2{=}CH.COOH + H_2O + O \rightarrow \underset{\text{Glyceric acid}}{CH_2OH.CHOH.COOH}$$

(*v*) *Polymerisation.* On standing it Polymerises slowly to a solid.

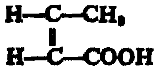
(*vi*) *Reactions of the carboxyl group*. It forms salts, esters and acid halides.

28. Crotonic Acid and Iso-crotonic Acid (*But-2-enoic acid*), **$CH_3CH{=}CH.COOH$.—Both of these acids have the same structure but are geometrical isomers.**



$$\begin{array}{c}\text{H—C—CH}_3\\ \|\\ \text{HOOC—C—H}\end{array}$$

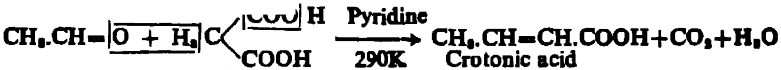
Crotonic acid
(*trans*-isomer)



$$\begin{array}{c}\text{H—C—CH}_3\\ \|\\ \text{H—C—COOH}\end{array}$$

Isocrotonic acid
(*cis*-isomers)

Crotonic acid is a more stable form and occurs as glyceryl ester in croton oil from which it derives its name. It is prepared by treating malonic acid with acetaldehyde in presence of pyridine (*Knoevenagel reaction*).



$$CH_3.CH{=}\boxed{O+H_2}C\begin{matrix}\diagup\boxed{COO}H\\ \diagdown COOH\end{matrix}\xrightarrow[290K]{Pyridine}CH_3.CH{=}CH.COOH+CO_2+H_2O$$

Malonic acid　　　Crotonic acid

It is a colourless crystalline substance (m.p. 345K) which gives general reactions of unsaturated acids.

Isocrotonic acid is a colourless liquid (f.p. 288K) which slowly changes into crotonic acid when heated at 370K.

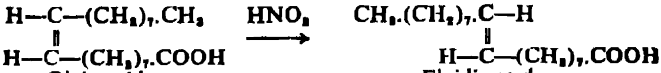
29. Oleic Acid, $CH_3(CH_2)_7.CH{=}CH(CH_2)_7.COOH$.—Oleic acid occurs as triolein (glyceryl ester) in oils and fats. It is a colourless oil (m.p. 280K) insoluble in water but soluble in alcohol and ether. Catalytic reduction of oleic acid gives stearic acid. Sodium or potassium salts of the acid are used as soaps. A few other reactions are :

(*i*) *Oxidation*. With acid permanganate it gives nonoic acid and azelaic acid.

$$\underset{\text{Oleic acid}}{C_{17}H_{33}COOH}\xrightarrow[KMnO_4]{acid}\underset{\text{nonoic acid}}{CH_3.(CH_2)_7.COOH}+\underset{\text{azelaic acid}}{COOH.(CH_2)_7.COOH}$$

This gives us the position of double bond and the information is further confirmed by ozonolysis.

(*ii*) *Action of nitrous acid*. When treated with nitrous acid, oleic acid changes into its geometrical isomer elaidic acid (*trans*-form—m.p. 324K).



$$\begin{array}{c}\text{H—C—(CH}_2)_7\text{.CH}_3\\ \|\\ \text{H—C—(CH}_2)_7\text{.COOH}\end{array}\xrightarrow{HNO_2}\begin{array}{c}\text{CH}_3\text{.(CH}_2)_7\text{.C—H}\\ \|\\ \text{H—C—(CH}_2)_7\text{.COOH}\end{array}$$

Oleic acid　(*cis*-form)　　Elaidic acid　(*trans*-form)

(*iii*) *Fusion with alkali*. When unsaturated acids are boiled with alkali the double bond migrates to αβ-position, *e.g.*,

$$CH_3CH{=}CH.CH_2.COOH\xrightarrow{NaOH}CH_3.CH_2.CH{=}CH.COOH$$

In fusion with alkali, the migration of double bond is followed by cleavage of the chain at the double bond, *e.g.*, oleic acid gives acetic and palmetic acids.

$$\underset{\text{Oleic acid}}{CH_3(CH_2)_7.CH{=}CH.(CH_2)_7.COOH}\xrightarrow[\text{migration of }(=)]{KOH}$$

$$\underset{\text{intermediate product}}{[CH_3(CH_2)_{14}.CH{=}CH.COOH]}\xrightarrow[\text{cleavage of chain}]{KOH}\underset{\text{(palmitic acid)}}{CH_3(CH_2)_{14}COOH}+\underset{\text{acetic acid}}{CH_3COOH}$$

QUESTIONS

Essay Type :

1. What general methods are available for the preparation of carboxylic acids ? Give an account of the more important reactions of these substances. *(Delhi B.Sc. 1967 ; Agra 1967)*

2. How is anhydrous formic acid prepared ? In what respects does it differ from acetic acid and why ? *(Punjab B.Sc. 1971)*

3. "The behaviour of first member of a homologous series is usually somewhat different from the behaviour of subsequent members of the series." Illustrate this with reference to formaldehyde and formic acid. *(Agra B.Sc. 1967)*

4. Give a brief account of the large-scale preparation of acetic acid. Starting from acetic acid how would you prepare ; (*i*) acetic anhydride ; (*ii*) acetyl chloride ; (*iii*) acetamide ? *(Agra B.Sc. 1967 ; Lucknow 1967)*

5. Discuss the structural formula of acetic acid.

6. Starting with acetic acid how will you prepare : (*i*) Trichloro-acetic acid ; (*ii*) Acetyl chloride ; (*iii*) Acetamide ; (*iv*) Acetic anhydride ; (*v*) Methane (*vi*) Methylamine ; (*vii*) Acetone ; (*viii*) Acetonitrile ; (*ix*) Ethane ; (*x*) Acetaldehyde : (*xi*) Malonic acid ; (*xii*) Aminoacetic acid ; and (*xiii*) Nitromethane *(Punjab B.Sc. 1961 ; Agra 1964 ; Gorakhpur 1965)*

7. (*a*) Account for the following :

(*i*) Molecular weight of acetic acid is double the calculated value.

(*ii*) Chloroacetic acid is stronger than acetic acid.

(*iii*) The carbonyl group in carboxylic acid does not react with phenylhydrazine. *(Delhi B.Sc. Hons. 1971, 70)*

(*b*) (*i*) Why are carboxylic acids stronger acids than alcohols.

(*ii*) Butyric acid is a weaker acid as compared with acetic acid.

8. Indicate how propionic acid could be converted into :

(*a*) Propionyl chloride,
(*b*) Propionaldehyde,
(*c*) α-Chloropropionic acid,
(*d*) Propionic anhydride,
(*e*) Lactic acid,
(*f*) Diethyl ketone,
(*g*) *n*-Butyric acid, and
(*h*) Acetaldehyde.

(Agra B.Sc. 1970 ; Madras 1976)

9. How is acrylic acid obtained from (*i*) acetylene, (*ii*) ethylene and (*iii*) a Grignard reagent ? How does it react with (*i*) HBr, and (*ii*) alkaline $KMnO_4$? *(Delhi B.Sc. 1976)*

10. How can formic acid be synthesised ? Show the presence of an aldehydic group, carboxyl group and a hydroxy group in its molecule. *(Delhi B.Sc. Hons. Sub. 1977)*

11. Discuss the structure of carboxylic group.

12. What is acidity of a carboxylic acid due to ? Why is it a stronger acid as compared to an alcohol ?

13. Discuss the effect of substituents on acidity of an acid.

Short Answer Type :

1. What is a carboxyl group ? Why is it so called ?

2. Lower carboxylic acids are very soluble in water. Solubility decreases with increase in molecular mass. Explain, why ?

3. Melting point of an acid with even number of carbon atoms is higher than those of its immediate neighbours with odd number of carbon atoms. How can you account for this fact ?

4. Boiling point of an acid is higher than an alcohol with same number of carbon atoms. Give reason, why ?

5. Which is more acidic of each pair :

(*a*) $CH_2ClCOOH$ and $CH_2BrCOOH$

(*b*) $CHCl_2COOH$ and CH_3COOH

(*c*) CH_3COOH and $HCOOH$

6. Complete the following equations :

(*i*) $C_2H_5MgBr \xrightarrow[(ii)\ H^+]{(i)\ CO_2}$

(*ii*) $C_2H_5COONa + NaOH \longrightarrow$

(*iii*) $CH_3CH_2COOH \xrightarrow{LiAlH_4}$

7. Arrange the acids given in each set in the order of increasing acidity

(*a*) CH_3CH_2COOH. $CH_3CHClCOOH$, $CH_3CHFCOOH$

(*b*) CH_3COOH, $CH_2ClCOOH$, $CHCl_2COOH$, CCl_3COOH

(*c*) $CH_3CHClCOOH$, CH_2ClCH_2COOH

8. In acrylic acid, $CH_2=CH—COOH$, the addition of HCl takes place contrary to Markownikoff's rule but in the acid with structure

$$CH_2=CH—CH_2—CH_2COOH,$$

the addition is in accordance with the rule. Explain. (*Delhi B.Sc. Hons. 1977*)

9. The labels of four bottles supposed to contain respectively acetone, formic acid, methyl alcohol and chloroform have been removed. By what chemical tests would you be able to put labels on these bottles ?

(*Jabbalpur B.Sc. 1976*)

10. Though fatty acids have $>C=O$ group in them, yet they do not form oximes. Explain. (*Delhi B Sc. Hons 1976*)

11. An alcohol does not dissociate to give hydrogen ions, while a carboxylic acid does, when both contain the hydroxyl group. Explain.

(*Delhi B.Sc. Hons Sub. 1977*)

12. β-Keto-acids undergo decarboxylation easily. Explain why.

(*Kerala B.Sc. 1975*)

13. Monochloro acetic acid is a stronger acid than monobromoacetic acid. Give reasons. (*Madurai B.Sc. 1976 Supp.*)

14. Starting from propionic acid how are the following prepared ?

(*i*) Propionamide, (*ii*) Propionic anhydride,

(*iii*) Diethyl ketone. (*Madurai B.Sc. 1976 Supp.*)

15. Formic acid is stronger acid than acetic acid. Explain, why.

(*Madurai B.Sc. 1976*)

16. Trichloroacetic acid is a stronger acid than acetic acid. Account for this. (*Madras B.Sc. 1976 Supp.*)

17. How is oxalic acid converted into formic acid ? (*Madras B.Sc. 1978*)

18. Give an example to illustrate reducing property of formic acid.

(*Madras B.Sc. 1978*)

19. How would you effect the following conversions ?

(*i*) 1-Bromopropane into butanoic acid ?

(*ii*) Malonic acid into acetic acid ? (*Madras B.Sc. 1978*)

20. How does acrylic acid react with

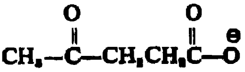
(*i*) bromine, (*ii*) dilute aqueous potassium permanganate ?

(*Madras B.Sc. 1978*)

21. Starting from acetic acid how will you obtain

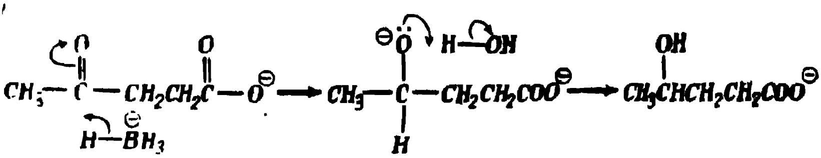
(*i*) monochloroacetic acid, (*ii*) acetamide ? (*Madras B.Sc. 1978*)

22. Predict the product of reduction of the following sodium salt of the keto acid with sodium borohydride in water.



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2CH_2\overset{\overset{O}{\|}}{C}-\overset{\ominus}{O}$$

Hint. Ketonic carbonyl group (>C=O) is sufficiently electrophilic to react with borohydride ion and get reduced to >CHOH. The carboxylate ion does not react due to delocalization.



23. Arrange the following acids according to their increasing strength, giving reasons :

(*i*) CH_3-O-CH_2COOH (*ii*) $CHCl_2-COOH$

(*iii*) CH_3COOH (*iv*) $NH_3 .\ CH_2-COOH$

(*Delhi B.Sc. Hons.' 1981*)

Problems :

1. A neutral compound containing 25·5% nitrogen after being heated with hydrochloric acid gave an acid containing 49·7% C and 8·1% H but no nitrogen.

0·2 g of this acid required for neutralization 27·0 cm³ of N/10-NaOH solution ; the vapour density of the ethyl ester=51. What is the neutral compound ?

2. Two organic substances A and B had the same percentage composition, carbon=40·00% and hydrogen=6·67%. The vapour density of A was 15 while that of B was 30. A reduced Fehling's solution but did not react with sodium carbonate, while B did not reduce Fehling's solution but produced effervescence with sodium carbonate. Deduce the structural formulae of A and B.

3. An organic compound A gave on analysis C=65·45%, H=9·1%, N=25·45%. On hydrolysis ammonia was liberated and the second substance B contained C=48·4%, and H=8·1%.

Calculate the formulae of A and B. Write equations representing the hydrolysis and also discuss the structural formula that you assign to A.

4. An organic ester A gave the following results on analysis :

(*a*) 0·15 g gave 0·22 g CO_2 and 0·09 g H_2O. The V.D. was 30.

(*b*) A on treatment with potassium hydroxide solution gave an alcohol B and potassium salt of an acid C.

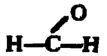
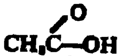
(*c*) B could be obtained by reduction of A and C by oxidation of B.

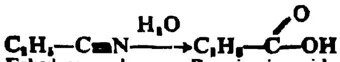
(*d*) C reduces silver nitrate. What structural formulae would you assign to A, B and C ? Explain these reactions.

5. A certain organic liquid contains C=48·66% ; H=8·11%. What is its empirical formula ? If the vapour density is 37, give all the possible formulae that the substance may have and give tests by which you will distinguish one from the other.

ANSWERS

1. $C_2H_5C\equiv N$ (*Ethyl cyanide*)

2. A is  $H-\overset{O}{\overset{\|}{C}}-H$ (*Formaldehyde*) ; B is  $CH_3\overset{O}{\overset{\|}{C}}-OH$ (*Acetic acid*)

3. 

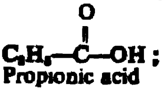
$C_2H_5-C\equiv N \xrightarrow{H_2O} C_2H_5-\overset{O}{\overset{\|}{C}}-OH$

Ethyl cyanide (A) Propionic acid (B)

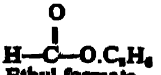
4. A is $HCOOCH_3$ (*Methyl formate*);
B is CH_3OH (*Methanol*) ;
C is HCOOH (*Formic acid*).

5. Empirical as well as Mol. formula = $C_3H_6O_2$

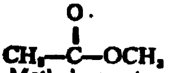
Possible isomers :



$C_2H_5-\overset{O}{\overset{\|}{C}}-OH$; Propionic acid



$H-\overset{O}{\overset{\|}{C}}-O.C_2H_5$ Ethyl formate



$CH_3-\overset{O}{\overset{\|}{C}}-OCH_3$ Methyl ace ate

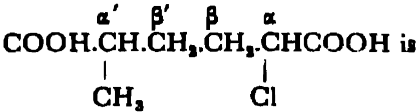
24

Dicarboxylic Acid

1. **Nomenclature.**—Saturated dicarboxylic acids are represented by the general formula $C_nH_{2n}(COOH)_2$ ($n=0$ for oxalic acid). Their common names generally indicate the source from which these have been obtained, *e.g.*, oxalic acid as it occurs in plants of the *oxalis* group. According to IUPAC system, their class suffix is *dioic acid or dicarboxylic acid* as shown below :

Formula	*Common name*	*IUPAC name*
$\begin{array}{l}COOH\\ \mid\\ COOH\end{array}$	Oxalic acid	Ethanedioic acid or Dicarboxylic acid
$CH_2\begin{array}{l}\diagup COOH\\ \diagdown COOH\end{array}$	Malonic acid	Propanedioic acid or Methanedicarboxylic acid
$\begin{array}{l}CH_2COOH\\ \mid\\ CH_2COOH\end{array}$	Succinic acid	Butanedioic acid or 1 : 2-ethane-dicarboxylic acid
$(CH_2)_3(COOH)_2$	Glutaric acid	Pentanedioic acid
$(CH_2)_4(COOH)_2$	Adipic acid	Hexanedioic acid
$(CH_2)_5(COOH)_2$	Pimelic acid	Heptanedioic acid
$(CH_2)_6(COOH)_2$	Suberic acid	Octanedioic acid
$(CH_2)_7(COOH)_2$	Azelaic acid	Nonanedioic acid
$(CH_2)_8(COOH)_2$	Sebacic acid	Decanedioic acid

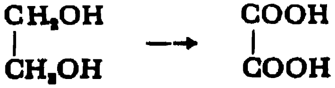
In the trivial system positions of side-chains are indicated by Greek letters and in the IUPAC system by numbers, *e.g.*,



$$\overset{\alpha'}{COOH.\underset{\substack{\mid\\ CH_3}}{CH}}.\overset{\beta'}{CH_2}.\overset{\beta}{CH_2}.\underset{\substack{\mid\\ Cl}}{\overset{\alpha}{CH}}COOH \text{ is}$$

α-chloro-α'-methyladipic acid (*Common name*) or 2-chloro-5-methylhexanedioic (*IUPAC name*)

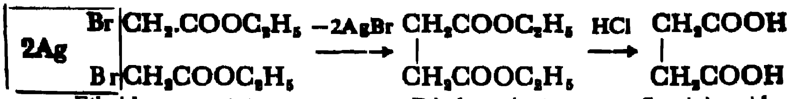
2. **General Methods of Preparation.**—(*i*) *By oxidation of glycols, e.g., ethylene* glycol gives oxalic acid.



$$\begin{array}{l}CH_2OH\\ \mid\\ CH_2OH\end{array} \longrightarrow \begin{array}{l}COOH\\ \mid\\ COOH\end{array}$$

Higher polymethylene glycols are inaccessible. This method is, therefore, not important.

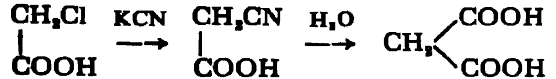
(*ii*) ***By treating halogen substituted esters of fatty acids with silver or zinc.***



$$2Ag + \begin{array}{l} BrCH_2.COOC_2H_5 \\ BrCH_2COOC_2H_5 \end{array} \xrightarrow{-2AgBr} \begin{array}{l} CH_2COOC_2H_5 \\ | \\ CH_2COOC_2H_5 \end{array} \xrightarrow{HCl} \begin{array}{l} CH_2COOH \\ | \\ CH_2COOH \end{array}$$

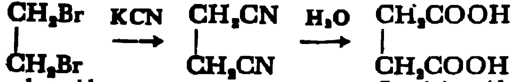
Ethyl bromoacetate Ethyl succinate Succinic acid

(*iii*) *Cyanide synthesis.* Starting material is polymethylene dibromide or a halogen-substituted acid.



$$\begin{array}{l} CH_2Cl \\ | \\ COOH \end{array} \xrightarrow{KCN} \begin{array}{l} CH_2CN \\ | \\ COOH \end{array} \xrightarrow{H_2O} CH_2\begin{array}{l} COOH \\ COOH \end{array}$$

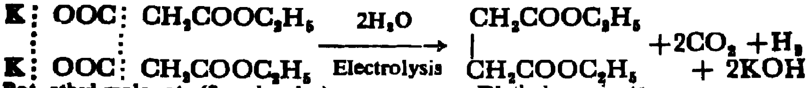
Chloro-acetic acid Malonic acid



$$\begin{array}{l} CH_2Br \\ | \\ CH_2Br \end{array} \xrightarrow{KCN} \begin{array}{l} CH_2CN \\ | \\ CH_2CN \end{array} \xrightarrow{H_2O} \begin{array}{l} CH_2COOH \\ | \\ CH_2COOH \end{array}$$

Ethylene bromide Succinic acid

(*iv*) *Crum-Brown and Walker electrolytic method.* Electrolysis of an aqueous solution of the potassium alkyl ester of a dibasic acid gives higher dicarboxylic acid.

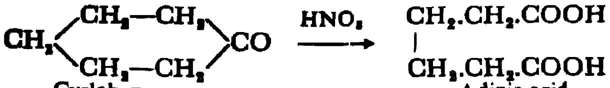


$$\begin{array}{l} K\vdots OOC\vdots CH_2COOC_2H_5 \\ K\vdots OOC\vdots CH_2COOC_2H_5 \end{array} \xrightarrow[\text{Electrolysis}]{2H_2O} \begin{array}{l} CH_2COOC_2H_5 \\ | \\ CH_2COOC_2H_5 \end{array} \begin{array}{l} +2CO_2 + H_2 \\ +\ 2KOH \end{array}$$

Pot. ethyl malonate (2 molecules) Diethyl succinate

(*v*) *By acetoacetic ester synthesis and better by malonic ester synthesis* (*see* Chapter 30).

(*vi*) *By oxidation of cyclic ketones.*



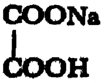
$$CH_2\begin{array}{l} CH_2—CH_2 \\ CH_2—CH_2 \end{array}CO \xrightarrow{HNO_3} \begin{array}{l} CH_2.CH_2.COOH \\ | \\ CH_2.CH_2.COOH \end{array}$$

Cyclohexanone Adipic acid

3. **General Properties.**—Dicarboxylic acids are crystalline solids soluble in water. Solubility decreases with increase in molecular weights. Their solubilities and melting points show alternation or oscillation from one member to the next. Odd acids (with odd number of carbon atoms) are more soluble in water than even acids (with even number of carbon atoms) immediately above and below them. Similarly even acids have higher melting points than the odd ones.

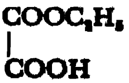
Chemical reactions of dibasic acids are mainly the reactions of the two carboxyl groups as given below :

(1) **Acidic Nature.** The acid strength of the dicarboxylic acids decreases as the series is ascended. They dissociate in two steps, the dissociation constant of the first being much greater than that of the second. They give two series of derivatives according as one or both carboxyl groups react. For example, possible derivatives of oxalic acid are :



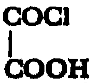
$$\begin{array}{l} COONa \\ | \\ COOH \end{array}$$

Acid sod. oxalate



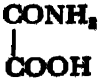
$$\begin{array}{l} COOC_2H_5 \\ | \\ COOH \end{array}$$

Acid ethyl oxalate



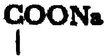
$$\begin{array}{l} COCl \\ | \\ COOH \end{array}$$

[Hypothetical]



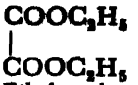
$$\begin{array}{l} CONH_2 \\ | \\ COOH \end{array}$$

Oxamic acid



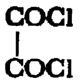
$$\begin{array}{l} COONa \\ | \\ COONa \end{array}$$

Sod. oxalate



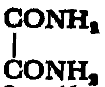
$$\begin{array}{l} COOC_2H_5 \\ | \\ COOC_2H_5 \end{array}$$

Ethyl oxalate



$$\begin{array}{l} COCl \\ | \\ COCl \end{array}$$

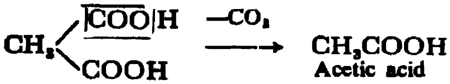
Oxalyl chloride



$$\begin{array}{l} CONH_2 \\ | \\ CONH_2 \end{array}$$

Oxamide

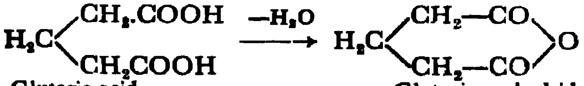
(2) **Action of Heat.** (*i*) Acids with two carboxyl groups attached to the same carbon atom eliminate a molecule of carbon dioxide on heating.



Malonic acid

Acetic acid

(*ii*) Succinic and glutaric acids on heating form cyclic anhydrides.

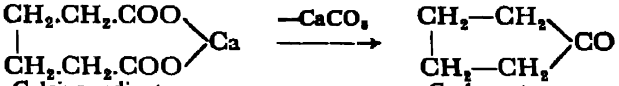


Glutaric acid

Glutaric anhydride

(*iii*) Adipic acid and higher members are stable towards heat.

(3) **Action of Heat on Calcium Salts.** Calcium salts of higher members form cyclic ketones when heated.



Calcium adipate

Cyclopentanone

(4) **Oxidation.** Except for oxalic acid, dicarboxylic acids are stable towards oxidising agents. This difference in behaviour is due to the fact that oxalic acid molecule has no hydrocarbon chain.

INDIVIDUAL MEMBERS

4. Oxalic acid (*Ethanedioic acid*), $(COOH)_2$.—Oxalic acid is one of the most important dicarboxylic acids and occurs in rhubarb, sorrel and other plants of the *oxalis* group (hence the name).

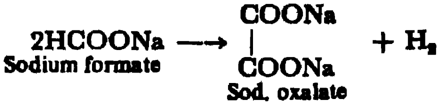
Preparation. (*i*) LABORATORY METHOD. Oxalic acid is prepared in the laboratory by oxidation of sucrose (cane-sugar) with concentrated nitric acid in the presence of vanadium pentoxide as catalyst. The product is concentrated and crystallized when oxalic acid crystals, $(COOH)_2 2H_2O$ separate which can be purified by recrystallization from water.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + 18O \xrightarrow[V_2O_5]{HNO_3} \underset{\text{Oxalic acid}}{6(COOH)_2} + 5H_2O$$

(*ii*) MANUFACTURE. An industrial method for the preparation of oxalic acid, which is now almost obsolete, is by heating strongly (470-490K) a paste of sawdust with caustic soda when sodium oxalate is obtained. The fused mass is treated with water when sodium oxalate dissolves. The solution is treated with milk of lime when calcium oxalate is precipitated which is filtered, washed and decomposed with sulphuric acid to recover oxalic acid. The precipitated calcium sulphate is filtered off and the filtrate evaporated to crystallization when oxalic acid dihydrate crystallizes out.

$$\underset{\text{Cal. oxalate}}{(COO)_2Ca} + H_2SO_4 \longrightarrow \underset{\text{ppt.}}{CaSO_4} + \underset{\text{Oxalic acid}}{(COOH)_2}$$

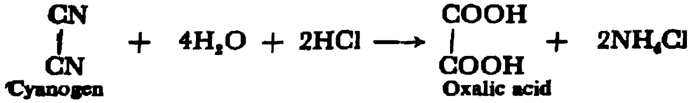
(*iii*) The modern method for the industrial preparation of oxalic acid is by heating sodium formate rapidly to 633K.



$$\underset{\text{Sodium formate}}{2HCOONa} \longrightarrow \underset{\text{Sod. oxalate}}{\begin{matrix} COONa \\ | \\ COONa \end{matrix}} + H_2$$

Sodium oxalate obtained is treated as described in method (*ii*) for obtaining free acid.

(*iv*) Oxalic acid can also be obtained by the hydrolysis of cyanogen with concentrated hydrochloric acid. The method is, however, of theoretical importance only.



$$\underset{\text{Cyanogen}}{\begin{matrix} CN \\ | \\ CN \end{matrix}} + 4H_2O + 2HCl \longrightarrow \underset{\text{Oxalic acid}}{\begin{matrix} COOH \\ | \\ COOH \end{matrix}} + 2NH_4Cl$$

(*v*) An interesting SYNTHESIS of oxalic acid is by heating sodium or potassium in a current of carbon dioxide at 633K.

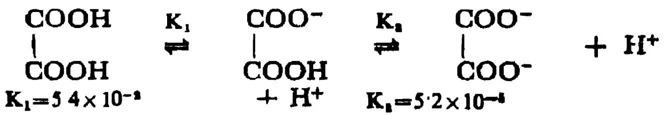
$$2Na + 2CO_2 \xrightarrow[633K]{} \underset{\text{Sod. oxalate}}{(COONa)_2}$$

5. Properties of Oxalic Acid.

(*a*) **Physical.** Oxalic acid is a colourless, crystalline solid with two molecules of water of crystallization. The hydrated acid melts at 374K whereas the anhydrous acid melts at 462·5K. It is poisonous in nature, soluble in water and alcohol but almost insoluble in ether.

(*b*) **Chemical.** Oxalic acid contains two carboxyl groups and gives the reactions of fatty acid in duplicate.

There being two ionizable hydrogen atoms, it ionizes in two steps. First hydrogen atom ionizes 1000 times more readily than the second hydrogen atom.



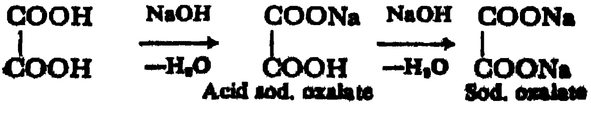
$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} \overset{K_1}{\rightleftharpoons} \begin{matrix} COO^- \\ | \\ COOH \end{matrix} + H^+ \overset{K_2}{\rightleftharpoons} \begin{matrix} COO^- \\ | \\ COO^- \end{matrix} + H^+$$

$$K_1 = 5.4 \times 10^{-2} \qquad K_2 = 5.2 \times 10^{-5}$$

This difference in K_1 and K_2 is due to the fact that more energy is needed in the second step when H^+ (proton) is being pulled away from the negatively charged $HOOC—COO^-$ ion than from the neutral molecule (in the first step).

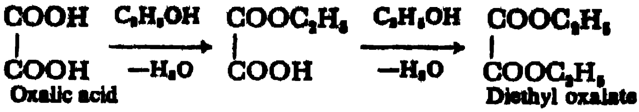
Some important reactions of oxalic acid are :

(*i*) **Neutralization.** With alkalis or carbonates it gives two series of salts.



$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} \xrightarrow[-H_2O]{NaOH} \underset{\text{Acid sod. oxalate}}{\begin{matrix} COONa \\ | \\ COOH \end{matrix}} \xrightarrow[-H_2O]{NaOH} \underset{\text{Sod. oxalate}}{\begin{matrix} COONa \\ | \\ COONa \end{matrix}}$$

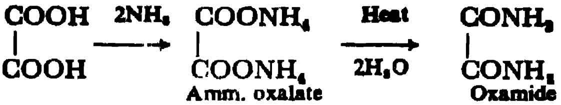
(*ii*) **Esterification.** With alcohols in the presence of conc. H_2SO_4, it gives two series of esters.



$$\begin{array}{c}COOH\\|\\COOH\end{array}\xrightarrow[-H_2O]{C_2H_5OH}\begin{array}{c}COOC_2H_5\\|\\COOH\end{array}\xrightarrow[-H_2O]{C_2H_5OH}\begin{array}{c}COOC_2H_5\\|\\COOC_2H_5\end{array}$$

Oxalic acid Diethyl oxalate

(*iii*) **With ammonia.** Ammonium oxalate is obtained when oxalic acid reacts with ammonia. This loses water on heating to give oxamide.



$$\begin{array}{c}COOH\\|\\COOH\end{array}\xrightarrow{2NH_3}\begin{array}{c}COONH_4\\|\\COONH_4\end{array}\xrightarrow[2H_2O]{Heat}\begin{array}{c}CONH_2\\|\\CONH_2\end{array}$$

Amm. oxalate Oxamide

(*iv*) **Action of Heat.** When heated, the dihydrate loses water at 370-378K, and when heated at about 470K, oxalic acid decomposes into carbon dioxide, carbon monoxide, formic acid and water.

$$(COOH)_2 \longrightarrow HCOOH + CO_2$$
$$(COOH)_2 \longrightarrow CO_2+CO + H_2O$$

(*v*) **With Glycerol.** When oxalic acid is heated with glycerol, formic acid or allyl alcohol is obtained depending upon the conditions of reactions (*see* page 2·162).

(*vi*) **Dehydration.** On heating with concentrated sulphuric acid at 360K, oxalic acid loses water giving carbon monoxide and carbon dioxide.

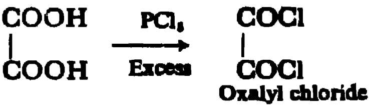
$$(COOH)_2 \xrightarrow{H_2SO_4,\ 360K} CO+CO_2+H_2O$$

(*vii*) **Oxidation.** With oxidising agents like acidified potassium permanganate, potassium dichromate or chlorine, it is oxidised to carbon dioxide.

$$(COOH)_2+O \longrightarrow 2CO_2+H_2O$$
$$(COOH)_2+Cl_2 \longrightarrow 2CO_2+2HCl$$

With concentrated nitric acid it is only very slowly oxidised.

(*viii*) **With Phosphorus pentachloride.** When oxalic acid is treated with excess of phosphorus pentachloride, the two —OH groups are replaced by two —Cl atoms and oxalyl chloride (b.p. 337K) is formed.

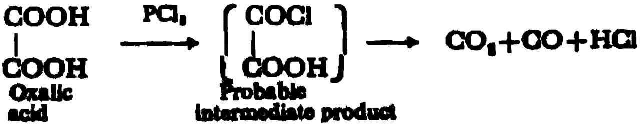


$$\begin{array}{c}COOH\\|\\COOH\end{array}\xrightarrow[Excess]{PCl_5}\begin{array}{c}COCl\\|\\COCl\end{array}$$

Oxalyl chloride

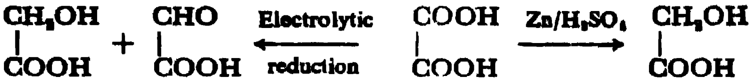
(*f.-p.*)

If an excess of phosphorus pentachloride is not used, oxalic acid decomposes instead of giving oxalyl chloride.



$$\begin{array}{c}COOH\\|\\COOH\end{array}\xrightarrow{PCl_5}\left[\begin{array}{c}COCl\\|\\COOH\end{array}\right]\longrightarrow CO_2+CO+HCl$$

Oxalic acid Probable intermediate product (*ix*) **Reduction.** Oxalic acid when reduced with zinc and sulphuric acid gives glycollic acid. Electrolytic reduction with lead cathode yields glycollic and glyoxylic acids.



$$\begin{matrix}CH_2OH\\|\\COOH\end{matrix} + \begin{matrix}CHO\\|\\COOH\end{matrix} \xleftarrow[\text{reduction}]{\text{Electrolytic}} \begin{matrix}COOH\\|\\COOH\end{matrix} \xrightarrow{Zn/H_2SO_4} \begin{matrix}CH_2OH\\|\\COOH\end{matrix}$$

Glyoxylic acid Oxalic acid Glycollic acid

6. **Uses.**—(*i*) Oxalic acid is used in volumetric analysis and is a constituent of most metal polishes.

(*ii*) It is used to remove ink stains from cloth and to bleach straw (for hats).

(*iii*) Its antimony salts are used as mordants in printing and dyeing.

(*iv*) Potassium ferrous oxalate is used in photography as a developer.

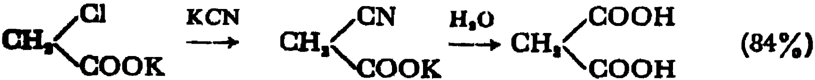
(*v*) For the laboratory preparation of allyl alcohol and formic acid.

7. **Tests.**—(*i*) The solid acid or its salts, when heated with concentrated sulphuric acid, yield without charring a mixture of carbon monoxide and carbon dioxide.

(*ii*) A neutral solution of oxalic acid gives with calcium chloride solution, a white precipitate of calcium oxalate insoluble in acetic acid.

(*iii*) Oxalic acid or its salt decolorises acidified potassium permanganate solution on warming.

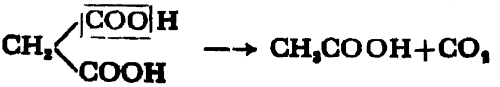
8. **Malonic Acid** (*Propanedioic acid*), $CH_2(COOH)_2$.—Malonic acid is commonly prepared by heating potassium chloroacetate with aqueous potassium cyanide followed by hydrolysis of the product (potassium cyanoacetate) with hydrochloric acid.



$$CH_2\begin{matrix}\diagup Cl\\ \diagdown COOK\end{matrix} \xrightarrow{KCN} CH_2\begin{matrix}\diagup CN\\ \diagdown COOK\end{matrix} \xrightarrow{H_2O} CH_2\begin{matrix}\diagup COOH\\ \diagdown COOH\end{matrix} \qquad (84\%)$$

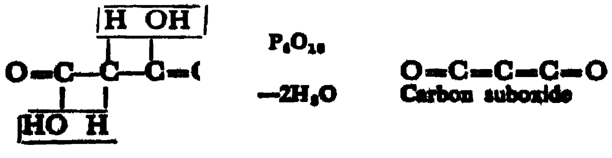
Potassium chloroacetate Potassium cyanoacetate Malonic acid

Malonic acid is a colourless, crystalline solid (m.p. 318·5K) soluble in water and alcohol but sparingly soluble in ether. It gives normal reactions of a dicarboxylic acid, *e.g.*, on heating to 413-423K, it eliminates a molecule of carbon dioxide to yield acetic acid.



$$CH_2\begin{matrix}\diagup \boxed{COO}H\\ \diagdown COOH\end{matrix} \longrightarrow CH_3COOH + CO_2$$

When malonic acid is heated with phosphorus pentoxide, a small amount of carbon suboxide is produced.



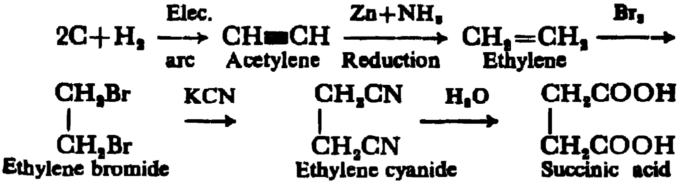
$$O{=}\underset{HO}{C}{-}\underset{H}{\overset{H}{C}}{-}\overset{OH}{C}{=}O \xrightarrow[-2H_2O]{P_4O_{10}} O{=}C{=}C{=}C{=}O$$

Carbon suboxide

Its diethyl ester (*malonic ester*) is a valuable synthetic reagent in organic chemistry.

9. Succinic Acid (*Butanedioic acid*), **$HOOC.CH_2CH_2.COOH$.** —It was originally obtained by distillation of amber called *succinum* in Latin (hence the name). It is also formed during the fermentation of sugar, etc.

Synthesis of Succinic Acid



$$2C+H_2 \xrightarrow[\text{arc}]{\text{Elec.}} \underset{\text{Acetylene}}{CH\equiv CH} \xrightarrow[\text{Reduction}]{Zn+NH_3} \underset{\text{Ethylene}}{CH_2=CH_2} \xrightarrow{Br_2}$$

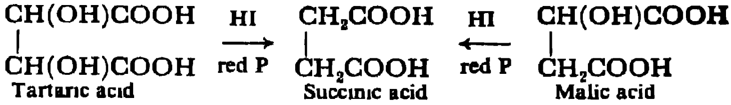
$$\underset{\text{Ethylene bromide}}{\begin{array}{l}CH_2Br\\|\\CH_2Br\end{array}} \xrightarrow{KCN} \underset{\text{Ethylene cyanide}}{\begin{array}{l}CH_2CN\\|\\CH_2CN\end{array}} \xrightarrow{H_2O} \underset{\text{Succinic acid}}{\begin{array}{l}CH_2COOH\\|\\CH_2COOH\end{array}}$$

Preparation. (*i*) *From ethylene bromide* as given above.

(*ii*) *By the reaction between malonic ester and ethyl chloroacetate or iodine* (*see* Chapter 30).

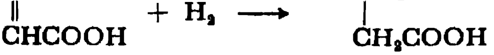
Manufacture. (*i*) It is prepared on a large scale as a by-product during the distillation of amber. The distillate is evaporated to dryness and crystallized from hot dil. HNO_3.

(*ii*) *Tartaric acid and malic acid on reduction by heating with hydriodic acid and red phosphorus in a sealed tube yield succinic acid.*



$$\underset{\text{Tartaric acid}}{\begin{array}{l}CH(OH)COOH\\|\\CH(OH)COOH\end{array}} \xrightarrow[\text{red P}]{HI} \underset{\text{Succinic acid}}{\begin{array}{l}CH_2COOH\\|\\CH_2COOH\end{array}} \xleftarrow[\text{red P}]{HI} \underset{\text{Malic acid}}{\begin{array}{l}CH(OH)COOH\\|\\CH_2COOH\end{array}}$$

(*iii*) *By the catalytic or electrolytic reduction of maleic acid.*



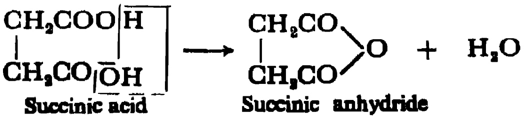
$$\begin{array}{l}CHCOOH\\\|\\CHCOOH\end{array} + H_2 \xrightarrow{Ni} \begin{array}{l}CH_2COOH\\|\\CH_2COOH\end{array}$$

Properties of Succinic Acid.

(*a*) **Physical.** It is a crystalline solid (m.p. 458K) moderately soluble in water and alcohol but sparingly soluble in ether.

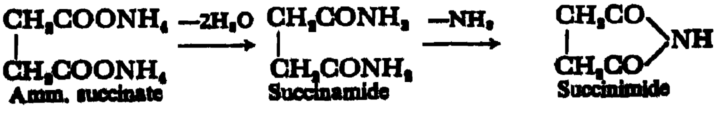
(*b*) **Chemical.** Succinic acid gives the normal reactions of dicarboxylic acid. A few more important reactions are :

(*i*) On heating, a large amount of succinic acid sublimes, the rest loses a molecule of water to give succinic anhydride.



$$\underset{\text{Succinic acid}}{\left.\begin{array}{l}CH_2COO|H\\|\\CH_2CO|OH\end{array}\right]} \longrightarrow \underset{\text{Succinic anhydride}}{\left.\begin{array}{l}CH_2CO\\|\\CH_2CO\end{array}\right>O} + H_2O$$

(*ii*) On heating ammonium succinate, we get succinamide which on further heating loses a molecule of ammonia to give succinimide.

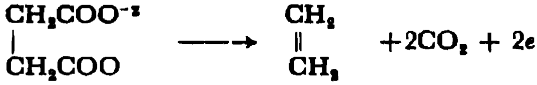


$$\underset{\text{Amm. succinate}}{\begin{array}{l}CH_2COONH_4\\|\\CH_2COONH_4\end{array}} \xrightarrow{-2H_2O} \underset{\text{Succinamide}}{\begin{array}{l}CH_2CONH_2\\|\\CH_2CONH_2\end{array}} \xrightarrow{-NH_3} \underset{\text{Succinimide}}{\left.\begin{array}{l}CH_2CO\\|\\CH_2CO\end{array}\right>NH}$$

(*iii*) On electrolysis of an aqueous solution of sodium or potassium succinate ethylene is obtained.

At cathode : $2H_2O+2e^- \longrightarrow 2OH^- + H_2$

At anode :

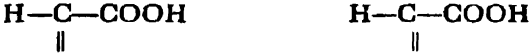


$$\begin{array}{l} CH_2COO^{-} \\ | \\ CH_2COO \end{array} \longrightarrow \begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array} + 2CO_2 + 2e^-$$

Uses. Succinic acid finds use in volumetric analysis, medicine and in the manufacture of dyes and perfumes.

UNSATURATED DICARBOXYLIC ACIDS

10. Introduction.—The formula of the simplest unsaturated dibasic acid is HOOC.CH=CH.COOH. In fact this formula respresents two important isomers, *viz.*, maleic acid and fumaric acid.



$$\begin{array}{c} H-C-COOH \\ \| \\ H-C-COOH \end{array} \qquad \begin{array}{c} H-C-COOH \\ \| \\ HOOC-C-H \end{array}$$

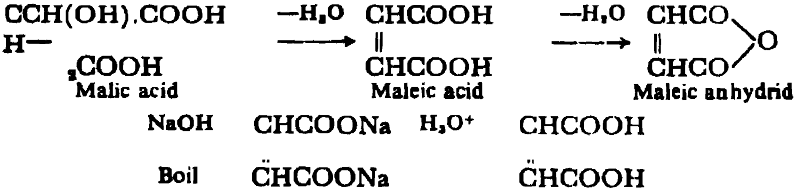
Cis *Trans*

Maleic acid which gives anhydride on heating is the *Cis* variety and fumaric acid is the *Trans* variety. Thus, we find that maleic and fumaric acids show *Geometrical isomerism* (*see page 1·184*).

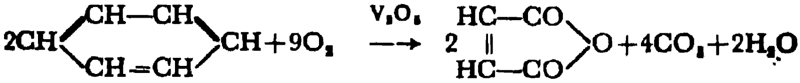
11. Maleic Acid.

Preparation. Maleic acid is a synthetic compound and does not occur in nature. It may be prepared :

(*i*) *By heating malic acid at about 520K. The maleic anhydride formed is converted into the acid by boiling with alkali and then acidifying.*



(*ii*) *By oxidation of benzene with air in the presence of vanadium pentoxide catalyst heated to 680-700K.*

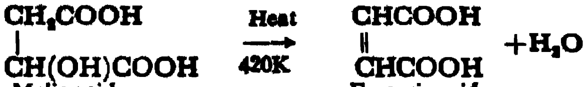


The anhydride so obtained is hydrolysed as before.

Properties. It is a colourless, crystalline solid (m.p. 403K) soluble in water. On heating a part of the acid distils unchanged and the rest changes into maleic anhydride. The anhydride is also obtained when the acid is heated with acetic anhydride. When heated for some time at 423K, it changes into fumaric acid. Its chemical properties have been described under fumaric acid.

12. Fumaric Acid.—Fumaric acid occurs in nature in many plants.

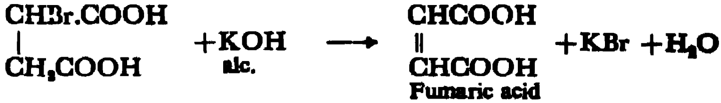
Preparation. (*i*) ***By heating malic acid at 420K for a long time.***



$$\begin{array}{l}CH_2COOH\\ |\\ CH(OH)COOH\end{array} \xrightarrow[420K]{Heat} \begin{array}{l}CHCOOH\\ \|\\ CHCOOH\end{array} + H_2O$$

Malic acid Fumaric acid

(*ii*) *By heating bromosuccinic acid with alcoholic potash,* maleic acid is also obtained.



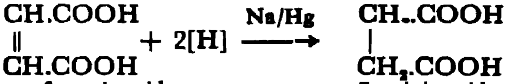
$$\begin{array}{l}CHBr.COOH\\ |\\ CH_2COOH\end{array} + \underset{alc.}{KOH} \longrightarrow \begin{array}{l}CHCOOH\\ \|\\ CHCOOH\end{array} + KBr + H_2O$$

Fumaric acid

Properties. It is a colourless crystalline solid (m.p. 560K) slightly soluble in water. It does not give the anhydride of its own but gives maleic anhydride when heated at 500K.

Chemically both fumaric and maleic acids give the reactions of alkenes as well as dibasic acids. For example,

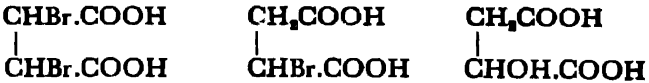
(*i*) *Reduction.* Both of them give succinic acid when reduced catalytically or with sodium amalgam.



$$\begin{array}{l}CH.COOH\\ \|\\ CH.COOH\end{array} + 2[H] \xrightarrow{Na/Hg} \begin{array}{l}CH_2.COOH\\ |\\ CH_2.COOH\end{array}$$

Maleic or fumaric acid Succinic acid

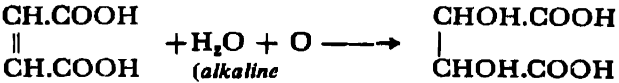
(*ii*) *Addition reactions.* Both of them form addition products with bromine and hydrobromic acid. A molecule of water is added on boiling it with dilute sulphuric acid under pressure and we get malic acid.



$$\begin{array}{l}CHBr.COOH\\ |\\ CHBr.COOH\end{array} \qquad \begin{array}{l}CH_2COOH\\ |\\ CHBr.COOH\end{array} \qquad \begin{array}{l}CH_2COOH\\ |\\ CHOH.COOH\end{array}$$

Dibromosuccinic acid (with Br_2) Bromosuccinic acid (with HBr) Malic acid (with H_2O)

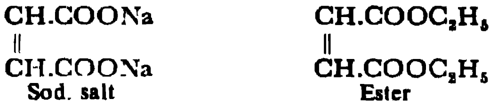
(*iii*) *Oxidation.* Both of them are oxidised by alkaline permanganate to tartaric acid.



$$\begin{array}{l}CH.COOH\\ \|\\ CH.COOH\end{array} + \underset{(alkaline\ permanganate)}{H_2O + O} \longrightarrow \begin{array}{l}CHOH.COOH\\ |\\ CHOH.COOH\end{array}$$

Maleic or fumaric acid Tartaric acid

(*iv*) *Formation of salts and esters.* Both of them form salts with alkalis and esters with alcohols.



$$\begin{array}{l}CH.COONa\\ \|\\ CH.COONa\end{array} \qquad \begin{array}{l}CH.COOC_2H_5\\ \|\\ CH.COOC_2H_5\end{array}$$

Sod. salt Ester

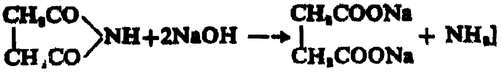
QUESTIONS

Essay Type :

1. What are general methods of obtaining dibasic acids ? How can you distinguish between methylmalonic acid, succinic acid, succinic anhydride and succinimide by simple chemical methods ?

[**Hint** : (*i*) Heat the sample. Methylmalonic acid decomposes liberating carbon dioxide. Succinic acid loses water to give the anhydride. Others are stable towards heat.

(*ii*) On heating with alkali succinimide decomposes liberating ammonia gas.



$$\begin{array}{l}CH_2CO\\ |\\ CH_2CO\end{array}\!\!>NH+2NaOH \longrightarrow \begin{array}{l}CH_2COONa\\ |\\ CH_2COONa\end{array} + NH_3$$

2. How is the oxalic acid obtained ? Mention its properties and uses Which properties distinguish it from other saturated dibasic acids ?

3. Describe the preparation and properties of succinic acid.

4. Contrast fumaric and maleic acids, making clear their nature of isomerism as well as the principal transitions between them.

5 Give the relationship between : (*i*) succinic acid ; (*ii*) malic acid . (*iii*) maleic acid ; and (*iv*) fumaric acid.

Describe how succinic acid can be converted into maleic acid. How is malic acid converted into maleic and fumaric acids ? Discuss the structure of maleic and fumaric acids.

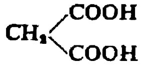
6. (*a*) How is malonic acid synthesised ? Describe the action of heat on the acid.

(*b*) Describe isomerism of fumaric acid and maleic acids and a method to determine configuration of these isomers.

Short Answer Type :

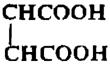
1. Write common as well as IUPAC names for the following compounds : (*i*) $(CH_2)_2(COOH)_2$; (*ii*) $(CH_2)_4(COOH)_2$

(*iii*)



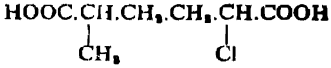
$$CH_2\!\!<\!\!\begin{array}{l}COOH\\ COOH\end{array}$$

(*iv*)



$$\begin{array}{l}CHCOOH\\ |\\ CHCOOH\end{array}$$

(*v*)



$$\begin{array}{l}HOOC.\underset{\displaystyle CH_3}{\underset{|}{CH}}.CH_2.CH_2.\underset{\displaystyle Cl}{\underset{|}{CH}}.COOH\end{array}$$

2. What is the action of alkaline $KMnO_4$ on—

(*i*) maleic acid, (*ii*) fumaric acid ?

(*Delhi B.Sc. 1976*)

3. Based on the orbital concept of covalent bond explain the existence of geometric isomers. (*Delhi B.Sc. 1976*)

4. What is the action of heat on the following :

(*i*) Malonic acid, (*ii*) Glutaric acid,

(*iii*) Oxalic acid, (*iv*) Ammonium oxalate,

(*v*) Ammonium succinate, (*vi*) Malic acid ?

5. How is oxalic acid converted into formic acid ?

(*Madras B.Sc. 1977*)

6. Explain the action of heat on (*i*) Succinic acid and (*ii*) Adipic acid. (*Madras B.Sc. 1978*)

7. How is oxalic acid obtained commercially ? (*Madras B.Sc. 1978*)

8. Indicate one use of oxalic acid in industry. (*Madras B.Sc. 1978*)

9. Starting from malic acid how would you prepare maleic and fumaric acids ? (*Delhi B.Sc. Hons. Sub. 1978 Supp.*)

10. How would you distinguish between maleic and fumaric acid ? (*Madras B.Sc. 1974* ; *Delhi B.Sc. Hons. Sub. 1978 Supp.*)

11. How will you obtain (*i*) succinic acid from ethylene ?

(*ii*) malonic acid from acetic acid ? (*Madras B.Sc. 1978*)

12. What products are obtained when malic acid is

(*i*) oxidised and (*ii*) reduced. (*Madras B.Sc. 1978*)

13. First hydrogen atom in oxalic acid ionizes 1000 times more readily than the second hydrogen atom. Explain why ?

Problems :

1. An organic compound $C_4H_6O_4$ (A) when heated with acetic anhydride gives another compound $C_4H_4O_3$ (B) which in turn reacts with ammonia to give a third compound $C_4H_5O_2N$ (C). Both B and C may be hydrolysed to A. With chlorine A gives a monochloro-compound D which reacts with caustic potash to give either $C_4H_4O_5K_2$ (E) or $C_4H_2O_4K_2$ (F) depending upon the condition of the reaction. Identify the compounds A to E.

2. A dibasic acid gave on analysis the following :

(*a*) 0·182 g gave on combustion 0·231 g of CO_2 and 0·063 g of water.

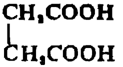
(*b*) 1·1113 g of its silver salt gave on ignition 0·756 g of silver metal.

Assign a formula to the acid and suggest a method for synthesising it.

3. Two grams of a substance of empirical formula $C_2H_3O_2$ neutralize 33·9 cm^3 of N-NaOH solution. The substance when heated with methyl alcohol and hydrochloric acid gas is converted into a neutral compound containing C, 49·3% and H, 6·84% with a V.D. of 73. What formula or formulae is or are possible for the substance and how would you distinguish between them ?

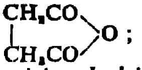
4. A dibasic organic acid gave the following results on analysis : 0·2496 g of acid gave 0·3168 g CO_2 and 0·0864 g H_2O. 0·1092 g of acid was neutralized by 21 cm^3 of N/10-NaOH exactly. Calculate the molecular formula of the acid and write down its structural formula.

ANSWERS

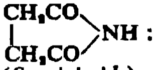
1 A is 

$$\begin{matrix}CH_2COOH\\|\\CH_2COOH\end{matrix}$$

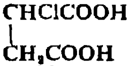
; (*Succinic acid*)

B is 

; (*Succinic anhydride*)

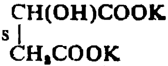
C is 

: (*Succinimide*)

D is 

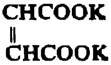
$$\begin{matrix}CHClCOOH\\|\\CH_2COOH\end{matrix}$$

; (*Monochlorosuccinic acid*)

E is 

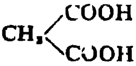
$$\begin{matrix}CH(OH)COOK\\|\\CH_2COOK\end{matrix}$$

(*Pot. malate*)

is 

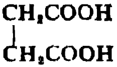
$$\begin{matrix}CHCOOK\\\|\\CHCOOK\end{matrix}$$

(*Pot. fumarate or Pot. maleate*)

2. 

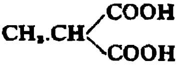
$$CH_2\begin{matrix}\nearrow COOH\\\searrow COOH\end{matrix}$$

(*Malonic acid*)

3. 

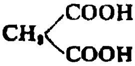
$$\begin{matrix}CH_2COOH\\|\\CH_2COOH\end{matrix}$$

Succinic acid

and 

$$CH_3.CH\begin{matrix}\nearrow COOH\\\searrow COOH\end{matrix}$$

Methylmalonic acid

4. 

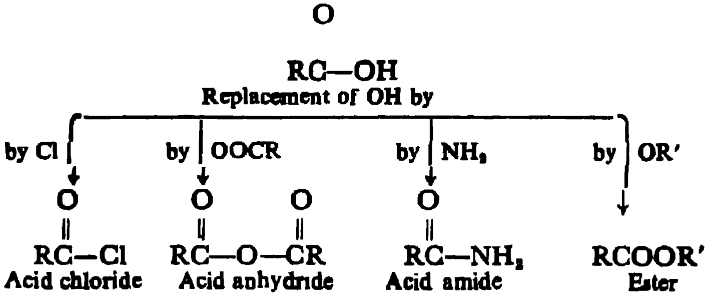
$$CH_2\begin{matrix}\nearrow COOH\\\searrow COOH\end{matrix}$$

(*Malonic acid*)

25

Acid Derivatives

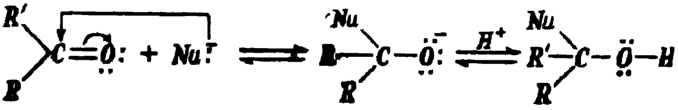
1. **Functional Derivatives of Carboxylic Acids.**—General formula of a monocarboxylic acid is RCOOH. Different compounds are obtained when OH group of the COOH group in it is replaced by $-Cl$, $-OOCR$, $-NH_2$ or $-OR'$. These are termed functional derivatives of carboxylic acids. Various derivatives are :



$R\overset{O}{C}$— group common to all the above derivatives is known as **acyl** group and these derivatives are termed **acyl compounds.**

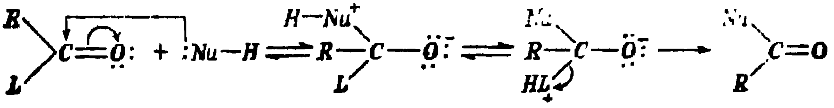
2. **Nucleophilic Substitution at Acyl Carbon.**—Before discussing various classes of acyl compounds individually, it will be instructive to discuss nucleophilic substitution at acyl carbon, a characteristic feature common to all of them.

Nucleophilic addition to the carbon-oxygen double bond ($>C=O$) is a characteristic reaction of aldehydes and ketones.



Aldehyde or ketone (*Nucleophilic addition*)

Carboxylic acids and their derivatives are characterized by nucleophilic substitution reactions taking place at the acyl carbon (carbonyl group) in each.



An acyl compound
L=Cl, OOCR′, NH_2 or
OR′ (or even OH in acids)

Another acyl compound
(*Nucleophilic Substitution*)

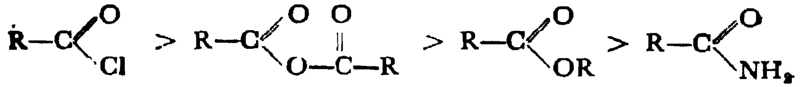
As shown above aldehydes and ketones undergo nucleophilic addition whereas acyl compounds undergo nucleophilic substitution. However, initial step in both reactions involves a nucleophilic attack on the carbonyl carbon. This attack is facilitated by the same two factors in each case :

(*i*) Relative steric openness of the carbonyl carbon.

(*ii*) Ability of the carbonyl oxygen to accommodate an electron pair of the carbon-oxygen double bond.

The two reactions, however, differ in the second step. The tetrahedral intermediate obtained in the case of aldehydes and ketones usually accepts a proton to yield an addition product. On the other hand the tetrahedral intermediate formed in the case of acyl compound usually ejects the leaving group leading to the regeneration of carbon-oxygen double bond and formation of a substitution product.

3. **Relative Reactivity of Acyl Compounds.**—The relative reactivities of various acyl compounds have been found to be in the following order :

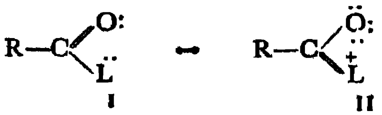


This overall order of reactivity can be accounted for in terms of the following three factors :

(*i*) Basicity of the leaving group, (*ii*) resonance effects and (*iii*) inductive effects.

(*a*) *Effect of the Basicity of Leaving group. Weaker bases are good leaving groups.* Hence acid derivatives with weaker bases as leaving groups are more reactive. Chloride ion being weakest base, acyl chlorides are most reactive of the acid derivatives. Amines are the strongest bases (as compared to Cl^-, ^-OOCR, ^-OR), hence amides are least reactive as given above.

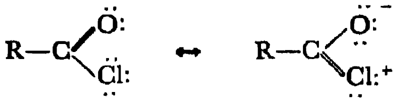
(*b*) *Resonance effect.* The leaving group in each has an atom with lone pair of electrons adjacent to the carbonyl group. The compound exists, therefore, as a resonance hybrid.



I II

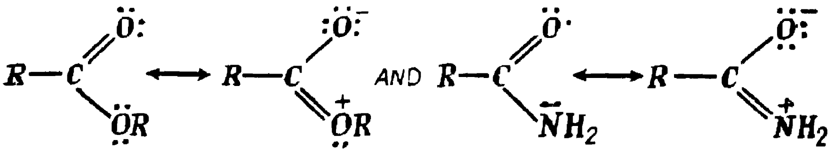
This results in the stabilization of the molecule as a whole and strengthening of the bond between carbon and the leaving group (it is C=L in **II**). The greater the stabilization, the smaller the reactivity of the acyl compound.

Acyl chlorides are least affected by resonance since it requires overlap of a $2p$ orbital of carbon with $3p$-chlorine orbital and the s orbitals being of different sizes, overlap is not large (*ineffective overlap*).



Being least stabilized, acid chlorides are most reactive.

Much more stabilization is caused by resonance in esters and amide since it involves more favourable overlap of $2p$ orbital of carbon with $2p$ orbital of oxygen in esters and $2p$ orbital of nitrogen in amides.

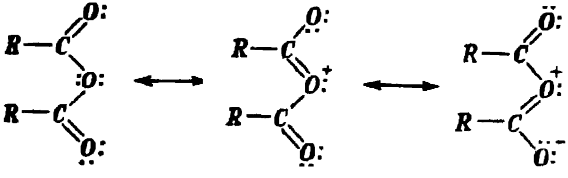


Ester Amide

As a result of more stabilization, esters and amides are least reactive.

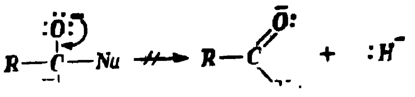
(*c*) *Inductive effect.* Between an ester and an amide, the inductive effect of oxygen in ester is greater than that of nitrogen in amide, hence ester is more reactive than an amide.

An acid anhydride is also stabilized by resonance as the orbital overlap is favourable. However, the stabilization of a particular carbonyl group is less than that of an ester since the resonance effect is shared between two carbonyl groups as shown below :

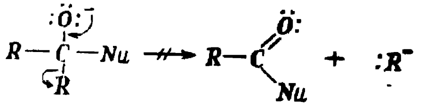


Synthesis of Acyl Compounds. As we shall see in the methods of preparation of different acid derivatives, in many cases one acid derivative is synthesised through a nucleophilic substitution reaction of another. The order of reactivities of various acid derivatives given above will be of great help in predicting as to which synthesis is practical and which is not. In general *less reactive acyl compounds can be prepared from more reactive ones.* The reverse is usually difficult and possible only when special conditions and/or a catalyst are employed.

Why do Aldehydes and Ketones not undergo Nucleophilic Substitution ? For an aldehyde or ketone to react by nucleophilic substitution would involve an ejection of a hydride ion (:H⁻) or an alkanide (:R⁻) by the tetrahedral intermediate. Both of these being powerful bases are very poor leaving groups. Hence the reaction does not occur.



Hydride ion

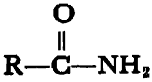


Alkanide ion

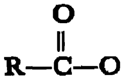
(Both these reactions are not feasible)

4. **Nucleophilic Substitution at Alkyl and Acyl Carbons.**—In alkyl halides nucleophilic substitution is taking place at the alkyl carbon while in acyl halides it occurs at the acyl carbon. The latter are more reactive than the former.

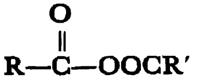
In general $R-\overset{\diagup O}{C}-L$ (an acyl compound) is more reactive than the corresponding R—L (an alkyl compound). For example



$R-\overset{\overset{\large O}{\|}}{C}-NH_2$ is more reactive than $R-NH_2$,

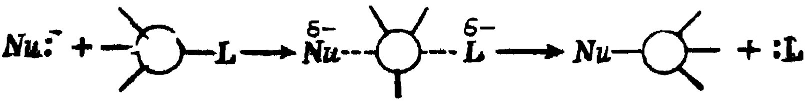


$R-\overset{\overset{\large O}{\|}}{C}-OR'$ is more reactive than $R-O-R'$, and



$R-\overset{\overset{\large O}{\|}}{C}-OOCR'$ is more reactive than $ROOCR'$.

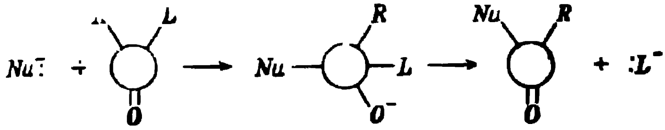
We can account for this difference in their reactivities by comparison of the S_N2 mechanism involved in each case. The nucleophilic attack on an alkyl carbon (*e.g.*, in R—X) involves a highly crowded and hence unstable transition state having a pentavalent carbon.



Tetrahedral carbon

Highly crowded transition state containing pentavalent carbon

On the other hand, the nucleophilic attack on trigonal acyl carbon (e.g., in RCOCl) involves a less crowded and hence more stable transition state which changes into a stable intermediate



Trigonal carbon

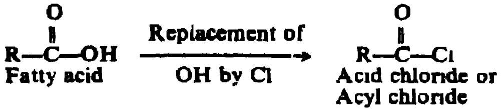
Intermediate state containing tetrahedral carbon

containing a tetravalent carbon. Moreover, attachment of the nucleophile to the acyl carbon involves the breaking of π bond of the C=O group and shifting of a negative charge to oxygen which can readily accept the same.

Thus greater reactivity of acyl compound is due to the presence of C=O group which is responsible for the ease of formation of the intermediate.

ACID OR ACYL CHLORIDES

5. Nomenclature.—Acid chlorides are obtained by the replacement of the hydroxyl in the carboxyl group by chlorine. These are also known as *acyl chlorides* because they contain the acyl group RCO—



$$\underset{\text{Fatty acid}}{R-\overset{\overset{O}{\|}}{C}-OH} \xrightarrow[\text{OH by Cl}]{\text{Replacement of}} \underset{\substack{\text{Acid chloride or}\\ \text{Acyl chloride}}}{R-\overset{\overset{O}{\|}}{C}-Cl}$$

The common names of acid chlorides are formed by changing the suffix -*ic* acid of the trivial names of the acids into -*yl* chloride, *e.g.*,

Formula	*Parent acid*	*Common names*
$HCOCl$	Formic acid	Formyl chloride
CH_3COCl	Acetic acid	Acetyl chloride
C_2H_5COCl	Propionic acid	Propionyl chloride
C_3H_7COCl	Butyric acid	Butyryl chloride

6. General Methods of Preparation.—Acid chloride may be prepared by the following general methods :

(*i*) *By heating the acid with phosphorus trichloride or pentachloride, e.g.*

$$3CH_3COOH + PCl_3 \rightarrow 3CH_3COCl + H_3PO_3 \qquad (g.)$$

$$\underset{\substack{\text{Propionic}\\ \text{acid}}}{C_2H_5COOH} + PCl_5 \rightarrow \underset{\substack{\text{Propionyl}\\ \text{chloride}}}{C_2H_5COCl} + POCl_3 + HCl \quad (v.g.)$$

(*ii*) *By the action of thionyl chloride on the acid.*

$$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\substack{\text{Thionyl}\\ \text{chloride}}}{SOCl_2} \rightarrow \underset{\substack{\text{Acetyl}\\ \text{chloride}}}{CH_3COCl} + SO_2 + HCl \qquad (v.g.)$$

(*iii*) *Acid chlorides are* **prepared industrially** *by distilling sodium salts of the acids which are cheaper, with phosphorus trichloride, phosphoryl chloride or sulphuryl chloride, e.g., acetyl chloride is pre- from sodium acetate.*

$$2CH_3COONa + POCl_3 \rightarrow 2CH_3COCl + NaCl + NaPO_3$$
$$2CH_3COONa + SO_2Cl_2 \rightarrow 2CH_3COCl + Na_2SO_4$$

7. General Properties of Acid Chlorides.—

Physical. Lower members are colourless, pungent-smelling liquids ; the higher members are colourless solids. They fume in moist air. These are insoluble in water but slowly dissolve on account of hydrolysis.

Chemical. The chlorine atom in acid chlorides is very reactive. This makes acid chlorides very important reagents. Various chemical reactions shown by them are :

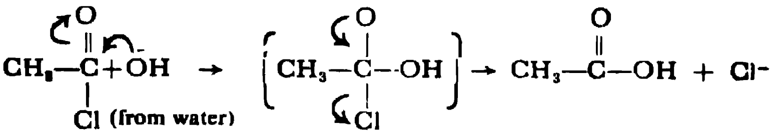
(*i*) **With hydroxy compounds.** When acid chlorides react with hydroxy compounds, *e.g.*, water, alcohol (ROH), the H-atom of the —OH group is replaced by acyl (—COR) group (*Acylation*). Acylation with acetyl chloride is termed acetylation.

$$\underset{\text{Water}}{HO\boxed{H + Cl}}\underset{\text{Acetyl chloride}}{COCH_3} \longrightarrow \underset{\text{Acetic acid}}{HOCOCH_3} + HCl$$

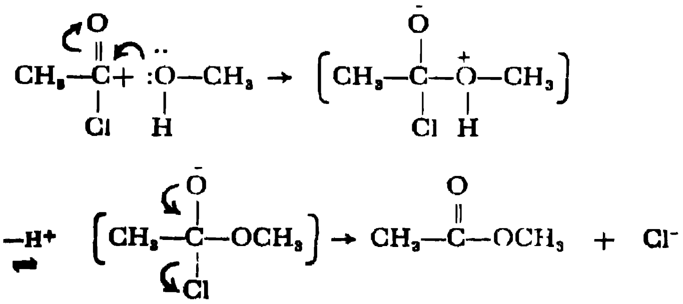
$$\underset{\text{Alcohol}}{RO\boxed{H + Cl}}COCH_3 \longrightarrow \underset{\text{Acetyl deriv. of alcohol (\textit{Ester})}}{RO.COCH_3} + HCl$$

The mechanism of the reaction is as follows :

With water—



With alcohols—

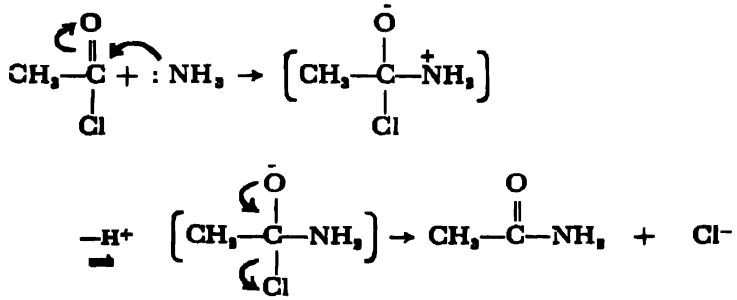


(*ii*) **With amino compounds.** Acylation occurs when acid chlorides react with amino compounds. During acylation H-atom of the amino group (—NH$_2$ or $>$NH) is replaced by an acyl (—COR) group.

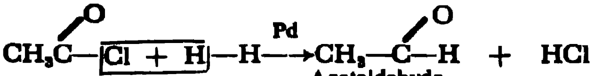
$$CH_3CO\boxed{Cl + H}\underset{\text{Ammonia}}{NH_2} \longrightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + HCl$$

$$\underset{\text{Amine}}{RNH}\boxed{{}_2 + Cl}\underset{\text{Acetyl chloride}}{COCH_3} \longrightarrow \underset{\text{Acetyl deriv. of the amine}}{RNH.COCH_3} + HCl$$

The mechanism of the reaction is as follows :

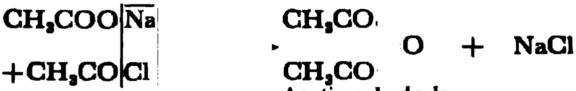


(*iii*) **Reduction.** Acid chlorides on reduction with hydrogen in presence of palladium suspended in $BaSO_4$ yield aldehydes (*Rosenmund's reaction*). For example, acetyl chloride on reduction gives acetaldehyde.



Acetaldehyde

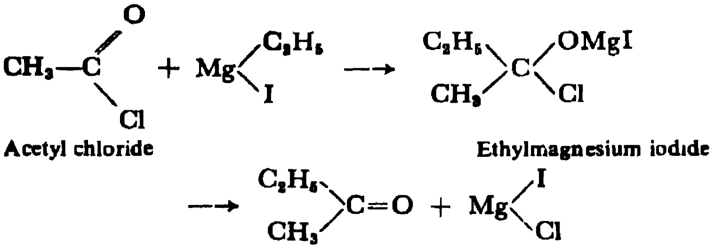
(*iv*) **Formation of Acid anhydrides.** When heated with sodium salt of a fatty acid, they give acid anhydride, *e.g.*, acetyl chloride with sodium acetate gives acetic anhydride.



$$CH_3COONa + CH_3COCl \longrightarrow (CH_3CO)_2O + NaCl$$

Acetic anhydride

(*v*) **With Grignard reagents.** Acid chlorides react with Grignard reagents to produce ketones, *e.g.*,



Acetyl chloride

Ethylmagnesium iodide

Ethyl methyl ketone

(*vi*) **Halogenation.** Acyl chlorides are readily halogenated in the α-position (see page 2·355).

(*vii*) **With carboxylic acids.** The acyl chlorides react as under:

$$RCOCl + R'COOH \rightleftharpoons RCOOH + R'COCl$$

In case R'COCl has lowest boiling point, whole of R'COOH may be converted to R'COCl.

(*viii*) **With Ethers.** Acetyl chloride reacts with ethers in the presence of zinc chloride to form alkyl acetate and alkyl chloride.

$$\underset{\text{Acetyl chloride}}{CH_3CO|Cl} + \underset{\text{Ether}}{C_2H_5|.O.C_2H_5} \longrightarrow \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + \underset{\text{Ethyl chloride}}{C_2H_5Cl}$$

(*ix*) **With potassium cyanide.** Acetyl chloride reacts with potassium cyanide to give acetyl cyanide which on hydrolysis yields pyruvic acid.

$$\underset{\text{Acetyl chloride}}{CH_3COCl} \xrightarrow{KCN} \underset{\text{Acetyl cyanide}}{CH_3COCN} \xrightarrow{H_2O} \underset{\text{Pyruvic acid}}{CH_3CO.COOH}$$

8. Formyl Chloride, HCOCl.—Formyl chloride is said to exist only at low temperatures (153K). A mixture of carbon monoxide and hydrogen chloride, however, behaves as if it were formyl chloride in certain reactions.

9. Acetyl Chloride, CH_3COCl.—It is the most important acyl halide.

Preparation. Acetyl chloride may be prepared by any of the general methods of preparation of acyl halides. It is, however, conveniently prepared by the action of phosphorus trichloride on glacial acetic acid (*Laboratory method*).

$$3CH_3COOH + PCl_3 \longrightarrow 3CH_3COCl + H_3PO_3$$

Expt. 40 ml of glacial acetic acid are taken in a distillation flask fitted with a dropping funnel and a water condenser carrying a dry receiver and a guard tube (Fig. 25·1). About 25 ml of phosphorus trichloride are dropped gently from the dropping funnel keeping the flask cool. It is then gently heated on a water bath to above 320K. The temperature is then raised when acetyl chloride distils over at 325K and is collected in the ice-cooled receiver.

Acetyl chloride so obtained is purified by redistillation.

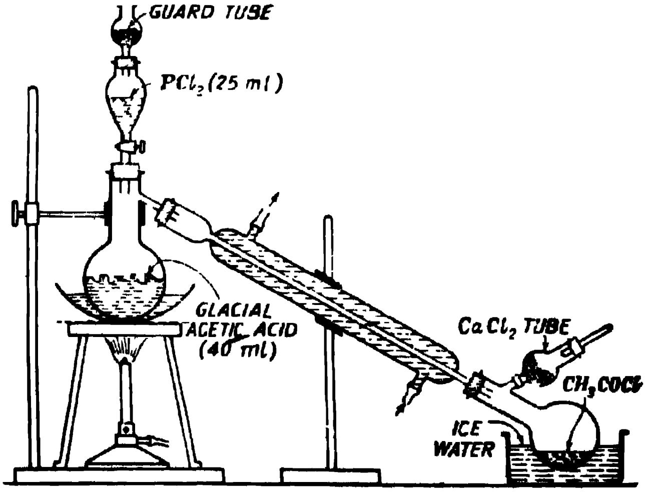


Fig. 25·1—Laboratory preparation of acetyl chloride.

Properties : (*a*) **Physical.** Acetyl chloride is a colourless, pungent-smelling, volatile liquid (b.p. 325K ; Sp. Gr. 1·104) which fumes in moist air.

(b) Chemical. It is a typical acid chloride and gives the general reactions of acyl chlorides.

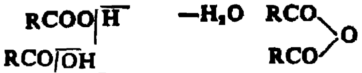
Uses. (i) For acetylation of alcohols and amines.

(ii) In organic synthesis.

(iii) For the detection of alcoholic and amino groups in organic compounds.

ACID ANHYDRIDES

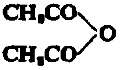
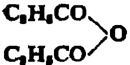
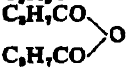
10. Nomenclature.—The anhydrides of the monobasic organic acids may be regarded theoretically as being derived from two molecules of the acid by the removal of one molecule of water.



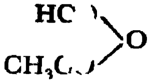
$$\begin{matrix}RCOO|H\\RCO|OH\end{matrix}\xrightarrow{-H_2O}\begin{matrix}RCO\\RCO\end{matrix}>O$$

Two molecules of an acid — Acid anhydride (General Formula)

These are named as the anhydrides of the acid radicals present, the trivial name of the acid being commonly used, *e.g.*,

Formula	*Parent acid*	*Common name*
 $\begin{matrix}CH_3CO\\CH_3CO\end{matrix}>O$	CH_3COOH Acetic acid	Acetic anhydride
 $\begin{matrix}C_2H_5CO\\C_2H_5CO\end{matrix}>O$	C_2H_5COOH Propionic acid	Propionic anhydride
 $\begin{matrix}C_3H_7CO\\C_3H_7CO\end{matrix}>O$	C_3H_7COOH Butyric acid	Butyric anhydride

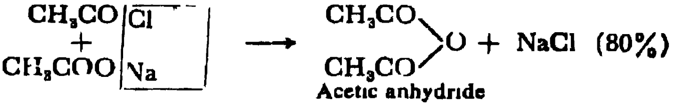
Formic anhydride is unknown but mixed anhydrides like formic acetic anhydride,



$\begin{matrix}HCO\\CH_3CO\end{matrix}>O$ are known.

11. Acetic Anhydride, $(CH_3.CO)_2.O$.—It is a typical representative of the homologous series.

Preparation. *Acetic anhydride is conveniently prepared in the* **laboratory** *by distilling a mixture of anhydrous sodium acetate and acetyl chloride.*



$$\begin{matrix}CH_3CO|Cl\\+\\CH_3COO|Na\end{matrix}\longrightarrow\begin{matrix}CH_3CO\\CH_3CO\end{matrix}>O+NaCl\ (80\%)$$

Acetic anhydride

Expt A small distillation flask is fitted with a dropping funnel and attached to a condenser and a receiver as shown in Fig. 25·1. The side-tube of the receiver is attached to a calcium chloride tube to arrest moisture. 50 g of powdered anhydrous sodium acetate are placed in the distillation flask and 40 g of acetyl chloride are placed in the dropping funnel. Acetyl chloride is slowly dropped into the distillation flask kept cool under water. When whole of the acetyl chloride has been added, the contents are thoroughly shaken and distilled when acetic anhydride distils over between 410K and 413K.

Manufacture. Acetic anhydride is prepared industrially :

(i) *By heating anhydrous sodium acetate with thionyl chloride, sulphuryl chloride or phosphoryl chloride* just enough to react with half of the sodium acetate. The inorganic chloride converts one-half of the sodium acetate into acetyl chloride which then reacts with unchanged sodium acetate to give acetic anhydride.

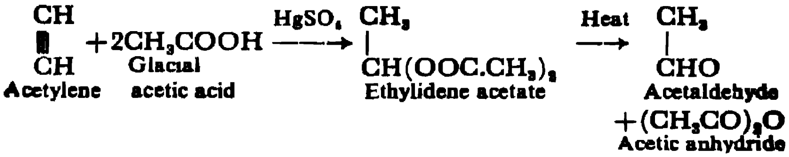
$$\underset{\text{Sodium acetate}}{CH_3COONa} + \underset{\text{Thionyl chloride}}{SOCl_2} \rightarrow \underset{\text{Acetyl chloride}}{CH_3COCl} + SO_2 + NaCl$$

$$\underset{\text{Acetyl chloride}}{CH_3COCl} + \underset{\text{Unchanged sod. acetate}}{CH_3COONa} \rightarrow \underset{\text{Acetic anhydride}}{(CH_3CO)_2O} + NaCl$$

(*ii*) *By passing chlorine in a mixture of sodium acetate and sulphur dichloride and distilling the mixture so obtained.*

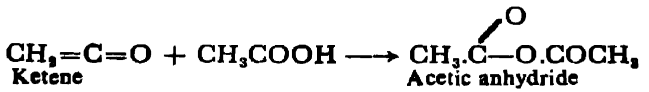
$$8CH_3COONa + \underset{\text{Sulphur dichloride}}{SCl_2} + 2Cl_2 \rightarrow \underset{\text{Acetic anhydride}}{4(CH_3CO)_2O} + 6NaCl + Na_2SO_4$$

(*iii*) *By passing acetylene into glacial acetic acid containing some mercuric sulphate (catalyst).* Ethylidene acetate produced is distilled to get acetic anhydride.



$$\underset{\text{Acetylene}}{\overset{CH}{\underset{CH}{\|}}} + \underset{\text{Glacial acetic acid}}{2CH_3COOH} \xrightarrow{HgSO_4} \underset{\text{Ethylidene acetate}}{\overset{CH_3}{\underset{CH(OOC.CH_3)_2}{|}}} \xrightarrow{\text{Heat}} \underset{\text{Acetaldehyde}}{\overset{CH_3}{\underset{CHO}{|}}} + \underset{\text{Acetic anhydride}}{(CH_3CO)_2O}$$

(*iv*) *By passing ketene into glacial acid.*



$$\underset{\text{Ketene}}{CH_2{=}C{=}O} + CH_3COOH \longrightarrow \underset{\text{Acetic anhydride}}{CH_3.\overset{\overset{O}{\diagup}}{C}{-}O.COCH_3}$$

Ketene is obtained by pyrolysis of acetone at high temperature (970-1020K).

$$\underset{\text{Acetone}}{CH_3.CO.CH_3} \longrightarrow \underset{\text{Ketene}}{CH_2{=}C{=}O} + CH_4$$

Anhydrides of higher fatty acids are prepared by heating the acid with acetic anhydride followed by fractionation. More volatile acetic acid distils over first.

$$\underset{\text{Higher fatty acid}}{2RCOOH} + \underset{\text{Acetic anhydride}}{(CH_3CO)_2O} \longrightarrow \underset{\text{Anhydride of higher acid}}{(RCO)_2O} + 2CH_3COOH$$

Properties : (*a*) **Physical.** Acetic anhydride is a colourless liquid (b.p. 412·5K) with a pungent smell resembling that of acetic acid. It is neutral when pure and is slightly soluble in water but readily dissolves in ether and benzene. Unlike acetyl chloride it does not fume in air.

(*b*) **Chemical.** Like acetyl chloride, acetic anhydride reacts with hydroxy and amino compounds, though with less vigour, forming their acetyl derivatives. One-half of the acetic anhydride molecule is used in acetylation while the other half is converted into acetic acid. Acetylation with acetic anhydride is best carried out in the presence of some sodium acetate or concentrated sulphuric acid (*catalysts*).

(*i*) **With hydroxy compounds.** The hydrogen atom of the hydroxyl group is replaced by acetyl group (*acetylation*).

$$\mathrm{HO|\overline{H + CH_3CO.O}|COCH_3 \rightarrow 2CH_3COOH}$$

Water Acetic anhydride Acetic acid

$$\mathrm{RO|\overline{H + CH_3CO.O}|COCH_3 \rightarrow RO.COCH_3 + CH_3COOH}$$

Alcohol Acetic anhydride Acetyl deriv. of alcohol (*ester*) Acetic acid

(*ii*) **With amino compounds.** Here again acetylation occurs and hydrogen atom of the amino group is replaced by the acetyl group.

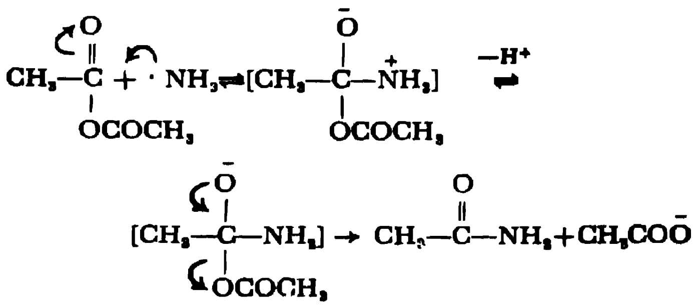
$$\mathrm{CH_3CO|\overline{O.COCH_3 + H}|NH_2 \rightarrow CH_3CONH_2 + CH_3COOH}$$

Acetic anhydride Ammonia Acetamide

$$\mathrm{(C_2H_5)_2N|\overline{H + CH_3CO.O}|COCH_3 \rightarrow (C_2H_5)_2N.COCH_3 + CH_3COOH}$$

Diethylamine Acetic anhydride Acetyl deriv. of diethylamine

The mechanism of the reaction with ammonia is :



(*iii*) **With dry hydrogen chloride.** Acetic anhydride reacts with dry hydrogen chloride to give acetyl chloride.

$$\mathrm{CH_3CO|\overline{O.COCH_3 + H}|Cl \rightarrow CH_3COCl + CH_3COOH}$$

Acetic anhydride Acetyl chloride Acetic acid

(*iv*) **With phosphorus pentachloride.** Acetic anhydride reacts with phosphorus pentachloride to give acetyl chloride.

$$\mathrm{(CH_3CO)_2O + PCl_5 \longrightarrow 2CH_3COCl + POCl_3}$$

Uses. Acetic anhydride is largely used :

(*i*) As an acetylating agent.

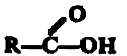
(*ii*) For the detection of hydroxy and amino groups.

(*iii*) In the manufacture of dyes and acetate rayon from cellulose.

(*iv*) In the manufacture of aspirin and some other pharmaceuticals.

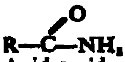
ACID AMIDES

12. Nomenclature.—**These are compounds in which the hydroxyl group present in the carboxyl group of an acid has been replaced by the amino group (—NH_2).**



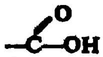
$\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}OH}$

Carboxylic acid



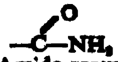
$\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}NH_2}$

Acid amide



$\mathrm{{-}\overset{O}{\overset{\|}{C}}{-}OH}$

Carboxyl group



$\mathrm{{-}\overset{O}{\overset{\|}{C}}{-}NH_2}$

Amide group

Their common names have been obtained by replacing the suffix *-ic acid* of the corresponding acid by *amide*. According to the IUPAC system, the final *e* of the parent alkane is replaced by *amide*.

Formula	*Parent acid*	*Common name*	*Parent alkane*	*IUPAC name*
$HCONH_2$	$HCOOH$ Formic acid	Formamide	Methane	Methanamide
CH_3CONH_2	CH_3COOH Acetic acid	Acetamide	Ethane	Ethanamide
$C_2H_5CONH_2$	C_2H_5COOH Propionic acid	Propionamide	Propane	Propanamide
$C_3H_7CONH_2$	C_3H_7COOH Butyric acid	Butyramide	Butane	Butanamide

13. **Formamide, $HCONH_2$.**—Formamide is prepared by heating ammonium formate in an atmosphere of ammonia.

$$\underset{\text{Am. formate}}{HCOONH_4} \longrightarrow \underset{\text{Formamide}}{HCONH_2} + H_2O$$

It is manufactured by the catalytic combination of ammonia and carbon monoxide under high pressure.

$$CO + \underset{\text{Ammonia}}{HNH_2} \longrightarrow \underset{\text{Formamide}}{HCONH_2}$$

Formamide is a hygroscopic liquid readily soluble in water and alcohol. It is unstable and readily decomposes at its boiling point. In this respect it differs from other amides.

$$HCONH_2 \longrightarrow CO + NH_3$$

It is an ionising solvent and dissolves many organic compounds.

In industry formamide is used as solvent, and as a plasticizer.

14. **Acetamide, Ethanamide, CH_3CONH_2.**

Preparation : (*i*) *By heating ammonium acetate.*

$$CH_3COONH_4 \longrightarrow CH_3CONH_2 + H_2O \qquad (g.\text{-}v.g)$$

Since ammonium acetate tends to dissociate on heating, the reaction is carried out in the presence of some free acetic acid which suppresses dissociation and hydrolysis of the salt. Acetamide is conveniently prepared in the laboratory by this method.

$$CH_3COONH_4 \rightleftharpoons CH_3COOH + NH_3$$

Expt. A mixture of ammonium acetate crystals and glacial acetic acid (equal weights) is taken in a round-bottom flask fitted with a long upright air condenser and refluxed for about 4 hours. Partial dehydration of ammonium acetate occurs to give acetamide and the water vapours escape through the condenser. The contents are transferred, while still hot, to a distillation flask and distillated using an air condenser. Acetamide distils over above 487K and the distillate solidifies on cooling. It may be further purified by recrystallization from alcohol and benzene.

(*ii*) ***By the action of concentrated solution of ammonia on acetyl chloride, acetic anhydride or ethyl acetate (ester).***

$CH_3COCl + 2NH_3 \rightarrow CH_3CONH_2 + NH_4Cl$ (*v.g.*)
Acetyl chloride Acetamide

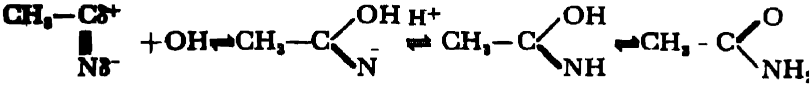
$(CH_3CO)_2O + 2NH_3 \rightarrow CH_3CONH_2 + CH_3COONH_4$ (*v.g.*)
Acetic anhydride Acetamide

$CH_3COOC_2H_5 + NH_3 \rightarrow CH_3CONH_2 + C_2H_5OH$ (*v.g.*)
Ethyl acetate Acetamide

(*iii*) ***By the partial hydrolysis of methyl cyanide*** effected by means of (*a*) alkaline hydrogen peroxide, or (*b*) by dissolving it in concentrated sulphuric acid and pouring the solution in cold water.

$$CH_3C\equiv N + H_2O \xrightarrow[\text{or } H_2SO_4]{\text{Alk. } H_2O_2} CH_3CONH_2$$

The mechanism of the reaction can be represented as under :



The methods used for the preparation of acetamide are also the general methods used for the preparation of other amides.

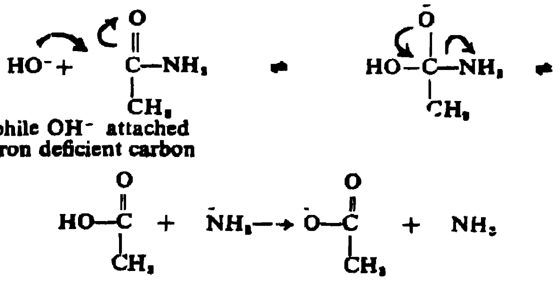
Properties : (*a*) **Physical.** Acetamide is a colourless crystalline solid (m.p. 335K ; b.p. 495K). It is practically odourless when pure. It is readily soluble in water, alcohol and ether.

(*b*) **Chemical.** (*i*) *Hydrolysis.* Acetamide is hydrolysed slowly by water, rapidly by acids and far more rapidly by alkalis.

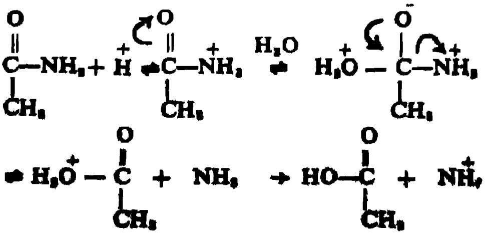
$$CH_3CO\overset{OH}{|}\overset{H}{NH_2} + H_2O \rightarrow CH_3COOH + NH_3$$

Mechanism of the Reaction

(*a*) *Basic hydrolysis of* CH_3CONH_2 :



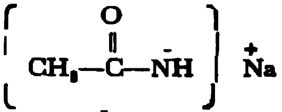
(*b*) *Acid hydrolysis of* CH_3CONH_2 :



(*ii*) ***Feebly Basic and Acidic Nature.*** The presence of acetyl group not only reduces the basic character of the amino group present but also makes the molecule feebly acidic. Acetamide is thus both feebly basic as well as acidic, *e.g.*, it forms unstable salts with strong inorganic acids (*feebly basic character*) and dissolves mercuric oxide to form covalent mercury compounds in which mercury is probably linked to the nitrogen (*feebly acidic character*).

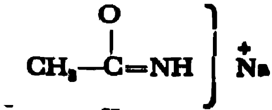
$$CH_3CONH_2 + HCl \rightarrow CH_3CONH_2.HCl$$
$$2CH_3CONH_2 + HgO \rightarrow (CH_3CONH)_2Hg + H_2O$$

When treated with sodium or sodamide in ethereal solution, the sodium salt $[CH_3CONH]^-Na^+$ is formed. The structure of the sodium salt may be **I** or **II**.



$$\left[CH_3-\overset{\overset{O}{\|}}{C}-\overset{-}{N}H\right]\overset{+}{Na}$$

I



$$\left[CH_3-\overset{\overset{O}{|}}{C}=NH\right]^{-}\overset{+}{Na}$$

II

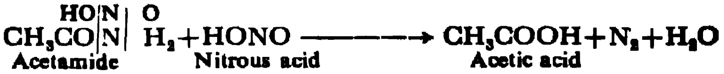
(*iii*) ***Reduction.*** Acetamide is reduced by sodium and ethanol or catalytically to ethylamine.

$$\underset{\text{Acetamide}}{CH_3CONH_2+4[H]}\xrightarrow{Na/C_2H_5OH}\underset{\text{Ethylamine}}{CH_3CH_2NH_2}+H_2O$$

(*iv*) ***Dehydration.*** Acetamide is dehydrated to methyl cyanide when heated with phosphorus pentoxide.

$$\underset{\text{Acetamide}}{CH_3CONH_2}\xrightarrow[-H_2O]{P_4O_{10}}\underset{\text{Methyl cyanide}}{CH_3C\equiv N}$$

(*v*) ***Action of Nitrous acid.*** When acetamide is treated with nitrous acid, nitrogen is evolved and acetic acid is formed.

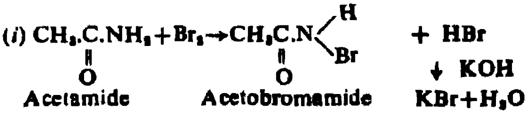


$$\begin{array}{llcl} \quad\ \ HO|N|\ O & & & \\ \underset{\text{Acetamide}}{CH_3CO|N|}\ H_2+\underset{\text{Nitrous acid}}{HONO} & \longrightarrow & \underset{\text{Acetic acid}}{CH_3COOH}+N_2+H_2O \end{array}$$

(*vi*) ***Hofmann Reaction or Hofmann Degradation.*** On treating an amide with bromine and alkali, a primary amine is obtained and has one carbon atom less than the amide. For example, acetamide gives methylamine. The reaction is known as Hofmann reaction or Hofmann degradation.

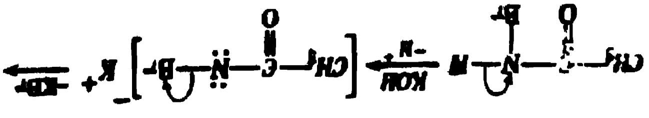
$$\underset{\text{Acetamide}}{CH_3CONH_2}+Br_2+4KOH\rightarrow\underset{\text{Methylamine}}{CH_3NH_2}+2KBr+K_2CO_3+2H_2O$$

The mechanism of the reaction is explained as follows :

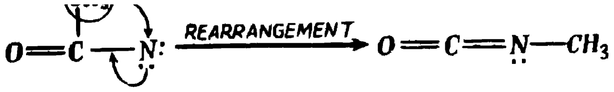


$$(i)\ \underset{\text{Acetamide}}{CH_3.\underset{\underset{O}{\|}}{C}.NH_2}+Br_2\rightarrow\underset{\text{Acetobromamide}}{CH_3\underset{\underset{O}{\|}}{C}.N\begin{smallmatrix}H\\Br\end{smallmatrix}}+\underset{KBr+H_2O}{\overset{HBr}{\downarrow\,KOH}}$$

(*ii*) Acetobromamide has acidic properties owing to the presence of the carbonyl group and the bromine atom. With KOH, it forms a salt which is unstable and loses a molecule of KBr and then undergoes molecular rearrangement to give methyl isocyanate. It is an example of 1, 2-shift.



(Acidic in nature) (Unstable salt)

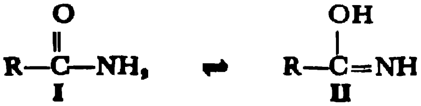


Methyl isocyanate

(*iii*) $CH_3.N{=}C{=}O + 2KOH \longrightarrow \underset{\text{Methylamine}}{CH_3NH_2} + K_2CO_3$

This reaction is used in the *Descent of series, i.e.*, for preparing a lower homologue from a higher one.

15. Structure of Amides.—To explain the amphoteric character of amides, it is assumed that they exist in two isomeric forms as given below :



$$\underset{\text{I}}{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH_2} \rightleftharpoons \underset{\text{II}}{R{-}\overset{\overset{\displaystyle OH}{|}}{C}{=}NH}$$

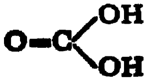
Form I is constantly changing into form II and *vice versa*. Thus it is a sort of dynamic isomerism caused by the wanderings of a labile hydrogen atom which oscillates like a pendulum between two polyvalent atoms—nitrogen and oxygen.

Form I contains a *keto group* (C=O) and is termed *keto form*. Form II is called *Enol form* due to the presence of an enol group (C=C—OH). **Enols** are compounds containing a double bond (C=C) as in alkenes and an OH group as in an alkanol.

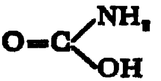
***This type of dynamic isomerism caused by the wanderings of a labile hydrogen atom between two polyvalent atoms in the same molecule is termed* Tautomerism or keto-enol tautomerism.** The isomers are called *tautomers* or *desmotropic forms*. The phenomenon is called *Desmotropy*.

In the amides, the keto form behaves as a weak base. The enol form, which is capable of giving metallic derivatives, behaves as a weak acid.

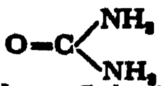
16. Amides of Carbonic acid.—Carbonic acid is a dibasic acid and gives two amides, the mono- and diamide. These are known respectively as carbamic acid and urea or carbamide.



Carbonic acid



Carbamic acid



Urea or Carbamide

17. Carbamic Acid, NH_2COOH.—The acid is unknown in free state, its salts and esters are, however, known. For example, (*a*) **Ammonium carbamate.** It is a white crystalline solid obtained when dry ammonia reacts with dry carbon dioxide.

$$2NH_3+CO_2 \longrightarrow NH_2.CO.ONH_4$$

It is very soluble in water and gives ammonium carbonate on hydrolysis when the aqueous solution is warmed to 330K.

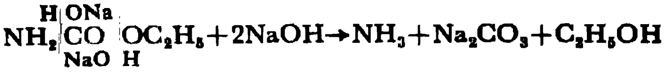
(*b*) **Urethan.** Esters of carbamic acid are called urethans. The ethyl ester is called urethan. It may be prepared by *treating ethyl chloroformate with ammonia.*

$$\underset{\text{Ethyl chloroformate}}{Cl.COOC_2H_5}+NH_3 \rightarrow \underset{\substack{\text{Ethyl carbamate}\\ \text{(Urethan)}}}{NH_2.COOC_2H_5}+HCl$$

Urethan is a crystalline solid (m.p. 323K) soluble in water, alcohol and ether. It reacts with ammonia to give urea.

$$\underset{\text{Urethan}}{NH_2CO|\underline{\overline{OC_2H_5 + \ \ H}}|NH_2} \rightarrow \underset{\text{Urea}}{NH_2CO.NH_2}+C_2H_5OH$$

It is decomposed when warmed with aqueous sodium hydroxide.



$$NH_2CO\,OC_2H_5+2NaOH \rightarrow NH_3+Na_2CO_3+C_2H_5OH$$

Urethan is a valuable hypnotic.

18. **Urea, Carbamide, $NH_2CO.NH_2$.**—Urea is the diamide of carbonic acid and is important physiologically. It is the final decomposition product of proteins and occurs in the urine. Adults excrete about 30 grams of urea per day in the urine. Its historical importance lies in its being the first organic compound synthesised in the laboratory in 1828 by Wohler.

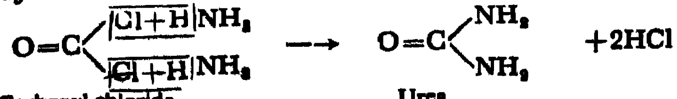
Preparation. (1) **From Urine.** Urea can be extracted from urine by evaporating it to a small bulk and adding nitric acid to precipitate sparingly soluble urea nitrate, $NH_2CO.NH_2.HNO_3$. From this urea is liberated with barium carbonate.

$$\underset{\text{Urea nitrate}}{2CO(NH_2)_2.HNO_3}+BaCO_3 \rightarrow \underset{\text{Urea}}{2CO(NH_2)_2}+Ba(NO_3)_2+CO_2+H_2O$$

(2) **Wohler's Synthesis.** By evaporating a solution, containing potassium cyanate and ammonium sulphate, ammonium cyanate which is formed first, undergoes molecular rearrangement (isomeric change) to give urea. Urea can be extracted from the residue with hot absolute alcohol and crystallized. It can be recrystallized from water.

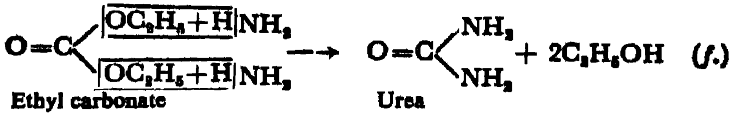
$$\underset{\text{Ammonium cyanate}}{NH_4CNO} \xrightarrow[\text{on heating}]{\substack{\text{Molecular}\\ \text{rearrangement}}} \underset{\text{Urea}}{NH_2.CO.NH_2}$$

(3) **Laboratory Method.** Urea may be prepared in the laboratory *by the action of ammonia* on carbonyl chloride or alkyl carbonate.



+2HCl (*i*)

Carbonyl chloride Urea



$$\underset{\text{Ethyl carbonate}}{O{=}C\begin{cases}\boxed{OC_2H_5+H}NH_2\\ \boxed{OC_2H_5+H}NH_2\end{cases}} \longrightarrow \underset{\text{Urea}}{O{=}C\begin{cases}NH_2\\ NH_2\end{cases}} + 2C_2H_5OH \quad (f.)$$

The constitution of urea as the diamide of carbonic acid follows from these syntheses.

(4) **Manufacture.** Industrially urea may be prepared :

(*i*) *By partial hydrolysis of cyanamide in feebly acidic solution.* Cyanamide is obtained from calcium cyanamide manufactured by passing nitrogen through heated calcium carbide at 1075K.

$$\underset{\substack{\text{Calcium}\\ \text{carbide}}}{CaC_2} \xrightarrow{N_2} \underset{\substack{\text{Calcium}\\ \text{cyanamide}}}{CaN.C{\equiv}N} \xrightarrow{H_2SO_4} \underset{\text{Cyanamide}}{H_2N.C{\equiv}N} \xrightarrow{H_2O} \underset{\text{Urea}}{H_2N.CO.NH_2}$$

(*ii*) By allowing liquid carbon dioxide and liquid ammonia to interact in an autoclave when ammonium carbamate is formed. This is heated to 400-450K under about 35 atmospheres pressure to get urea. The conversion is about 40 per cent.

$$2NH_3+CO_2 \rightarrow \underset{\text{Ammonium carbamate}}{NH_2.CO.ONH_4} \rightarrow \underset{\text{Urea}}{NH_2CO.NH_2}+H_2O$$

Properties. (*a*) **Physical.** Urea is a colourless, odourless solid (m.p. 405K) freely soluble in water and alcohol but insoluble in ether.

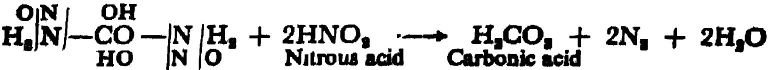
(*b*) **Chemical** : (*i*) *Basic Nature.* An aqueous solution of urea is neutral but behaves as a very weak monoacid base. A concentrated solution of urea reacts with strong nitric acid or concentrated solution of oxalic acid to give sparingly soluble urea nitrate, $CO(NH_2)_2.HNO_3$ and urea oxalate, $[CO(NH_2)_2]_2.H_2C_2O_4$ respectively.

(*ii*) *Biuret Reaction.* On heating gently, urea loses a molecule of ammonia to give *biuret.*

$$\underset{(\textit{Two molecules of Urea})}{NH_2CO\boxed{NH_2+\ H}NH.CO.NH_2} \xrightarrow[-NH_3]{\text{Heat}} \underset{\textit{Biuret}}{NH_2CO.NH.CO.NH_2}$$

When an aqueous solution of biuret is treated with sodium hydroxide solution and a drop of very dilute copper sulphate solution, a *violet coloration* is produced. The reaction is characteristic of all compounds containing —CO.NH— group.

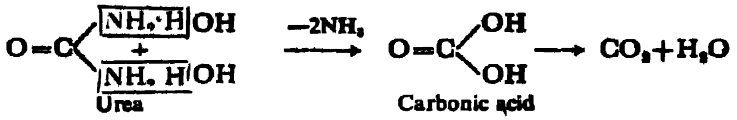
(*iii*) *Action with Nitrous Acid.* Urea reacts with nitrous acid with the liberation of nitrogen which, however, is not evolved quantitatively. The two amino groups of urea are replaced by two hydroxyl groups to give carbonic acid, H_2CO_3 which further decomposes to give carbon dioxide and water.



$$\begin{array}{l} \quad O|N|\quad OH\\ H_2|N|-CO-|N|H_2\\ \qquad\quad HO\ \ |N|O \end{array} + \underset{\text{Nitrous acid}}{2HNO_2} \longrightarrow \underset{\text{Carbonic acid}}{H_2CO_3} + 2N_2 + 2H_2O$$

$$H_2CO_3 \longrightarrow CO_2+H_2O$$

(*iv*) *Hydrolysis.* On boiling with aqueous alkalis or acids or water under pressure, urea hydrolyses to give carbon dioxide and ammonia.



$$\underset{\text{Urea}}{O{=}C\begin{matrix}\boxed{NH_2\,H}OH\\ +\\ \boxed{NH_2\,H}OH\end{matrix}} \xrightarrow[\quad]{-2NH_3} \underset{\text{Carbonic acid}}{O{=}C\begin{matrix}OH\\ OH\end{matrix}} \longrightarrow CO_2+H_2O$$

The enzyme *urease* (present in soyabeans) brings about the same change. The reaction is rapid and quantitative and thus serves as a method for the estimation of urea.

$$\underset{\text{Urea}}{CO(NH_2)_2}+2H_2O \rightarrow \underset{\text{Ammonium carbonate}}{(NH_4)_2CO_3} \rightarrow 2NH_3+CO_2+H_2O$$

(*v*) *Action of Alkaline Hypochlorite or Hypobromite.* Nitrogen is evolved though not quantitatively, when urea is treated with excess alkaline hypochlorite or hypobromite (Br_2+NaOH).

$$Br_2+2NaOH \longrightarrow NaBr+NaBrO+H_2O$$

$$\underset{\text{Urea}}{CO(NH_2)_2}+\underset{\substack{\text{Sodium hypobromite}\\ (\textit{Alkaline})}}{3NaBrO}+2NaOH \longrightarrow N_2+Na_2CO_3+3NaBr+3H_2O$$

Urea present in urine is roughly estimated by measuring the volume of nitrogen evolved.

(*vi*) *Acetylation.* Urea reacts with acid chlorides and acid anhydrides to form *ureides*, *i.e.*, with acetyl chloride it gives acetyl-urea.

$$\underset{\text{Acetyl chloride}}{CH_3CO\boxed{Cl+H}}\underset{\text{Urea}}{NH.CO.NH_2} \rightarrow \underset{\text{Acetylurea}}{CH_3CO.NH.CONH_2}+HCl$$

(*vii*) *Action with Hydrazine.* Urea reacts with hydrazine to give semicarbazide.

$$\underset{\text{Urea}}{NH_2.CO\boxed{NH_2+H}}\underset{\text{Hydrazine}}{NH.NH_2} \longrightarrow \underset{\text{Semicarbazide}}{NH_2.CO.NH.NH_2}+NH_3$$

(*viii*) *Pyrolysis.* When heated rapidly, ammonia is liberated and cyanic acid is produced which rapidly polymerises to cyanuric acid.

$$\underset{\text{Urea}}{CO(NH_2)_2} \xrightarrow[-NH_3]{\text{Heat}} \underset{\text{Cyanic acid}}{HOCN} \xrightarrow{\text{Polymerises}} \underset{\text{Cyanuric acid}}{(HOCN)_3}$$

Uses. (*i*) As a fertiliser.

(*ii*) In the manufacture of formaldehyde-urea plastics and various medicines, *e.g.*, veronal.

(*iii*) In the manufacture of hydrazine.

Tests. (*i*) On heating with sodium hydroxide solution, urea gives ammonia.

(*ii*) With strong nitric acid or a concentrated solution of oxalic acid, a concentrated aqueous solution of urea gives white crystalline precipitate of urea nitrate or urea oxalate.

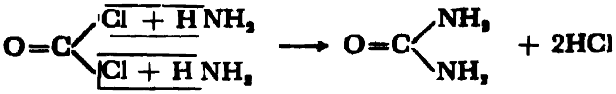
(*iii*) On adding sodium nitrite solution and dilute hydrochloric acid to urea solution, nitrogen gas is evolved.

(*iv*) Nitrogen is evolved by treating an aqueous solution of urea with sodium hypobromite solution (bromine water and caustic soda).

(*v*) Urea is also detected by *biuret reaction* (*see* page 2·272).

Structure. (*i*) Molecular formula of urea is CON_2H_4.

(*ii*) *Diamide formula.* Its formation from carbonyl chloride and ammonia suggests that urea has a symmetrical diamide formula.



$$O{=}C\left\langle\begin{matrix}\boxed{Cl+H}\,NH_2\\ \boxed{Cl+H}\,NH_2\end{matrix}\right.\longrightarrow O{=}C\left\langle\begin{matrix}NH_2\\NH_2\end{matrix}\right.+2HCl$$

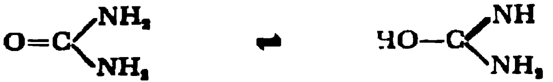
In some respects urea actually behaves like a diamide. For example, it gives ammonia on hydrolysis or pyrolysis. With nitrous acid nitrogen is liberated which indicates the presence of primary amino groups.

(*iii*) *Chattaway's Tautomeric structure.* The diamide structure fails to explain the following facts about urea.

(*a*) It forms stable salts with strong inorganic acids whereas amides do not form stable salts.

(*b*) It reacts with only one molecule of monobasic acid to form salts, *e.g.*, $CO(NH_2)_2.HCl$.

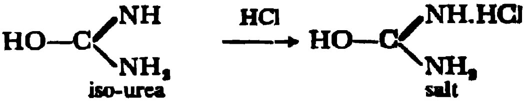
Chattaway explained this by assuming that urea occurs in tautomeric forms.



$$O{=}C\left\langle\begin{matrix}NH_2\\NH_2\end{matrix}\right.\rightleftharpoons HO{-}C\left\langle\begin{matrix}NH\\NH_2\end{matrix}\right.$$

Urea (*neutral amide*) iso-urea (*basic amidine*)

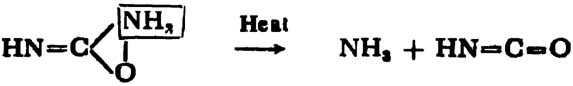
In the case of other amides, the amidine structure is not possible. Further amidines are much stronger bases than amides and it is the imide form which gives salts with acids.



$$HO{-}C\left\langle\begin{matrix}NH\\NH_2\end{matrix}\right.\xrightarrow{HCl}HO{-}C\left\langle\begin{matrix}NH.HCl\\NH_2\end{matrix}\right.$$

iso-urea salt

(*iv*) *Werner's formula.* To explain the ease with which urea loses ammonia to form cyanic acid, Werner suggested the following structure for urea :

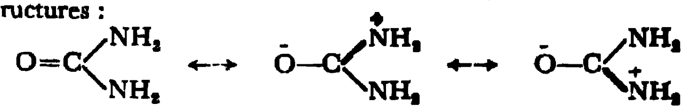


$$HN{=}C\left\langle\begin{matrix}\boxed{NH_3}\\ |\\ O\end{matrix}\right.\xrightarrow{Heat}NH_3+HN{=}C{=}O$$

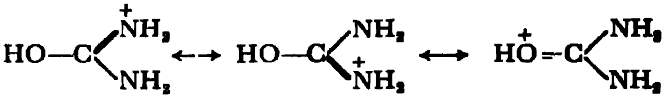
Werner's formula explained the addition of one molecule of hydrochloric acid due to the presence of strongly basic imido group —NH.

(*v*) *As a Resonance hybrid.* Crystal structure studies have shown that in solid urea both nitrogen atoms are identical as in the diamide formula.

Bond length measurements have shown the C—N distance in urea to be 1·37 Å which is intermediate between 1·47Å (for C—N in aliphatic amines) and 1·28 Å for C=N. This shows that C—N bond in urea has some double bond character (about 28%). This can be explained by assuming urea to be a resonance hybrid of the following structures :



In the hybrid molecule both the nitrogen atoms are identical. The negatively charged oxygen is capable of coordinating with one proton (H^+). Urea will, therefore, behave as a monoacid base. The salt may be formulated as a resonance hybrid.



Dipole moment work also confirms that urea is a resonance hybrid.

Estimation. (i) **Hufner's Method.** In a given solution urea is estimated by treating a known volume of the solution with excess of alkaline hypobromite solution (Br_2+NaOH) and measuring the volume of nitrogen evolved in a nitrometer.

$$\underset{60\text{ g}}{CO(NH_2)_2}+3NaBrO \rightarrow \underset{\substack{22.4\text{ litres}\\ \text{at NTP}}}{N_2} + CO_2+2H_2O+3NaBr$$

Expt A measured volume ($=x$ ml, say) of urea solution is taken in a small test tube and placed in the bottle *B* containing excess of freshly prepared

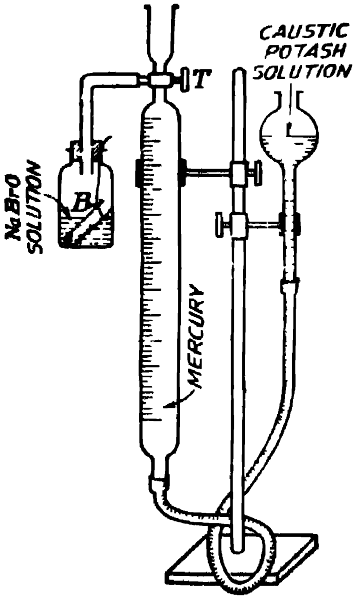


Fig. 25 2—Lunge's nitrometer.

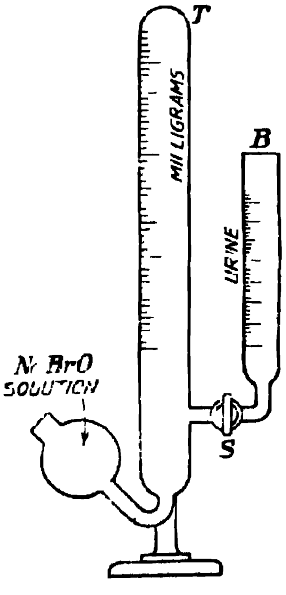


Fig. 25·3—Ureameter.

sodium hypobromite solution (Fig. 25·2). The nitrometer containing caustic potash solution is adjusted and put in communication with the reaction flask *B* by turning the tap *T*. On tilting the bottle *B* the reaction starts and nitrogen collects in the nitrometer while carbon dioxide is dissolved by caustic potash solution. The volume of nitrogen collected is noted and reduced to NTP (= *v* ml, say).

As indicated by the chemical equation, 22·4 litres of nitrogen at NTP are obtained from 60 g of urea. From this the amount of urea present in

v ml of the solution taken $= \frac{60}{22,400} \times v$ g

(*ii*) **Clinical Method.** A rapid estimation of urea in urine is carried out in clinical laboratories in a ureameter shown in Fig. 25·3.

Expt. The bigger tube T closed at upper end is filled with the freshly prepared hypobromite solution and urine is taken in the side tube. By opening the stopcock *S*, 1 ml of urine is introduced into *T*. Nitrogen evolved collects in T which is so graduated as to indicate directly the amount of urea present in *x* ml of urine or urea solution.

(*iii*) **Biochemical method.** The hypobromite method of estimating urea is not strictly accurate. In a more accurate method of urea estimation, urea is hydrolysed by the enzyme *urease* and the ammonia liberated is estimated volumetrically.

$$\underset{\text{Urea}}{CO(NH_2)_2} + H_2O \xrightarrow{\textit{Urease}} CO_2 + 2NH_3$$

The apparatus used for the purpose is shown in Fig. 25·4. Test-tube *A* contains water. *B* contains 5 ml of urine, 5 g of powdered soyabean and a little liquid paraffin (*to prevent frothing*). *B* is surrounded by hot water in the bath. *C* contains a known volume of some standard acid.

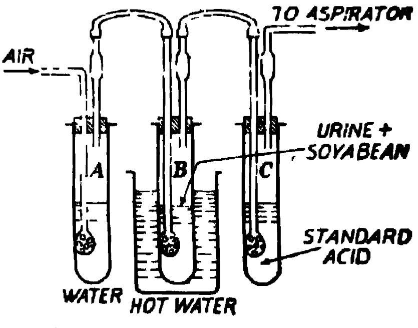


Fig. 25·4—Biochemical method for estimation of urea.

The apparatus is allowed to stand for 15 minutes and then the aspirator is worked on the right. A current of air passes through *A*, *B* and *C*. In *A* water dissolves any ammonia coming with air. The ammonia evolved in tube *B* is swept into the tube *C* by air coming from *A*. A part of the standard acid in *C* is neutralized by this ammonia. After about an hour about 5 g potassium carbonate is added to *B* to decompose any ammonium carbonate formed there. Ammonia evolved is again passed into *C* as before.

Finally, the acid left unused in *C* is estimated by back-titration against a standard alkali. Knowing the total acid taken and the volume of acid left unused we can calculate the volume of acid neutralized and the amount of ammonia needed for neutralisation. From this we can calculate the amount of urea present in 5 ml of urine taken using the relationship

34 g of ammonia ≡ 60 g of urea.

19. Thiourea, Thiocarbamide, $(NH_2)_2CS$.—Thiourea may be prepared by heating ammonium thiocyanate at 443K for some time.

$$NH_4CNS \longrightarrow (NH_2)_2C{=}S$$

It is a white crystalline solid (m.p. 453K) fairly soluble in water and alcohol. It behaves as a monoacid base. On heating with alkalis it is hydrolysed.

$$S{=}C(NH_2)_2 + 2H_2O \xrightarrow{NaOH} CO_2 + H_2S + 2NH_3$$

On oxidation with alkaline permanganate it yields urea.

$$S{=}C(NH_2)_2 + [O] \longrightarrow O{=}C(NH_2)_2 + S$$

Thiourea is used : (*i*) In the manufacture of plastics which are more stable and better water-resistant than the corresponding plastics.

(*ii*) To protect furs and clothing from insects.

(*iii*) As a reagent in the estimation of cadmium and lead.

20. Spectroscopic Analysis of Acid Derivatives.—

Infrared Spectra. In the IR spectra of an acid derivative there is strong C=O stretching absorption band with frequency depending upon the nature of the compound as shown below :

Compound	*Absorption band frequencies*
Acid chloride	1785-1815 cm^{-1} and C—Cl stretching band in the range 650-800 cm^{-1}
Acid anhydride	1800-1840 cm^{-1} ; 1740-1780 cm^{-1} In conjugated acid chlorides and anhydrides these bands occur at frequencies lower by 15-20 cm^{-1}.
Amides	1650-1690 cm^{-1} They also show N—H stretching bands at 3100-3500 cm^{-1} and also N—H bending bands ~1600 cm^{-1}
Saturated esters	1740 cm^{-1}
α, β-unsaturated esters	1715-1730 cm^{-1}

Esters and anhydrides also give strong C—O stretching bands in the region 1050-1300 cm^{-1}. This helps us to distinguish these from ketones.

NMR spectra. In the case of amides the protons of the —$CONH_2$ group absorb in the range τ 2-5 (δ 5-8) giving characteristic broad peaks.

There are two kinds of protons in esters : (*i*) those of alkyl group —OR and (*ii*) those of acyl group $R-\overset{\overset{\displaystyle O}{\|}}{C}-$. The former absorb more downfield τ 5·5-6·5 (δ 3·5-4·5) than the latter which absorb at τ 7·5-8 (δ 2-2·5).

QUESTIONS

A. **Essay Type :**

1. (*a*) How would you prepare acetyl chloride in the laboratory ? What happens when acetyl chloride reacts with :

(*i*) reducing agent, (*ii*) ethylmethylamine, (*iii*) sodium propionate, and (*iv*) isopropyl alcohol ? Mention its importance as a reagent.

(*b*) A substance of the formula $C_4H_{10}O_4$ yields on acetylation with acetic anhydride a derivative of the formula $C_{12}H_{18}O_8$. How many hydroxyl groups are present in the substance ? What is its probable structure ?

2. (*a*) How is urea manufactured ? What is the action of (*i*) nitrous acid, (*ii*) alkaline hypobromite on urea ?

(*b*) What is the difference in reactivity of the chlorine atom present in acetyl chloride and in chloroacetic acid ? (*Delhi B.Sc. 1972*)

3. Why is urea called carbamide ? How is urea prepared ? What are its characteristic reactions ? Discuss its constitution. What are its important uses ?

4. How is urea manufactured ? Describe the action of (*a*) heat, (*b*) nitrous acid, and (*c*) malonic ester on urea.

0·4 g of a sample of impure urea on treatment with alkaline sodium hypobromite gave 112·0 ml of nitrogen at NTP. Calculate the purity of the given samples of urea. (*Delhi B.Sc. 1971*)

5. (*a*) What is the natural source of urea ? How is urea synthesized ? What are its important uses ?

(*b*) Explain what happens when urea is—

(*i*) heated alone, (*ii*) heated with hydrazine, (*iii*) treated with alkaline hypobromite solution, (*iv*) treated with malonic ester, (*v*) treated with ice-cold nitrous acid. (*Delhi B.Sc. 1978*)

B. Short Answer Type :

1. Name the following compounds :

(*i*) C_3H_7COCl ;
(*ii*) $(C_2H_5CO)_2O$;
(*iii*) $CH_2{=}C{=}O$;
(*iv*) CH_3CONH_2 ;
(*v*) NH_2COOH ;
(*vi*) $(NH_2)_2C{=}O$;
(*vii*) $(NH_2)_2C{=}S$;
(*viii*) $NH_2COOC_2H_5$;
(*ix*) $NH_2CONH.CONH_2$;
(*x*) $NH_2CONH.NH_2$.

2. What is the action of (*i*) heat, (*ii*) sodium hypochlorite, (*iii*) nitrous acid and (*iv*) malonic ester on urea ? (*Delhi B.Sc. 1976*)

3. Give the mechanism of Hofmann hypobromite reaction. (*Delhi B.Sc. Hons. Sub. 1976*)

4. Explain briefly why acetyl chloride is a stronger acetylating agent than acetic acid. (*Delhi B.Sc. Hons. 1977*)

5. Why acetyl chloride is a better acetylating agent than acetic anhydride ? Explain, giving reasons. (*Delhi B.Sc. Hons. 1976*)

6. How is acetic anhydride obtained ?

7. Give reasons why acetamide is very slowly hydrolysed with water but rapidly in the presence of an acid or an alkali. (*Punjab B Sc. 1975 Supp.*)

8. Explain why Amides ($RCONH_2$) are much weaker bases (rather somewhat acidic) than amines. (*G.N.D. B.Sc. 1976 Supp.*)

9. Explain why S_N2 reaction takes place much readily at an acyl carbon than an alkyl carbon. (*G.N.D. B.Sc. 1976*)

10. Give the probable mechanism of the alkaline hydrolysis of an ester. (*Punjab B Sc. 1976 Supp.*)

11. Complete the equation given below, mentioning the name of the reaction concerned.

$$CH_3CONH_2 \xrightarrow{OH^-}$$

(*Punjab B.Sc. 1976 Supp.*)

12. What is Hofmann's degradation ? (*Madurai B.Sc. 1978, 77*)

13. How will you distinguish between acetamide and urea ? *(Kanpur B.Sc. 1978)*

14. How will you show that acetamide possesses an amide group ? *(Kanpur B.Sc. 1977)*

15. Write a note on Biuret reaction. *(Madras B.Sc. 1978)*

16. Explain why urethane is prepared by the reaction of isocyanate and absolute ethyl alcohol. *(Delhi B Sc. 1978)*

C. Problems :

1. An organic compound A (C_4H_9NO) on treatment with bromine and alkali forms another compound B (C_3H_9N). On treatment with sodium nitrite and dilute hydrochloric acid, B yields C (C_3H_8O). C can be oxidised to D (C_3H_6O) which can also be synthesised from methyl acetylene.

Identify the compounds A to D and write the reactions involved. *(Delhi B.Sc. 1976 Supp.)*

2. A white solid containing C, H, N, and O was found to give the following results on analysis :

$$C=40{\cdot}6\%\ ;\ H=8{\cdot}5\%\ ;\ N=23{\cdot}7\%.$$

The vapour density of the substance was found to be 29·5. On heating the substance with alkali, ammonia was evolved. Suggest the probable structure of the compound.

3. With bromine and caustic potash the straight chain compound C_4H_9ON (A) gives C_3H_9N (B), with caustic soda, $C_4H_7O_2Na$ (C) and with phosphorus pentaoxide, C_4H_7N (D).

With hydrochloric acid D gives $C_4H_8O_2$ (E) of which C is the sodium salt. B may be converted to an alcohol F and thence to a halide, the Grignard reagent from which reacts with carbon dioxide to give E. On oxidation F gives successively C_3H_6O (G) and $C_3H_6O_2$ (H).

Identify the compounds A to H.

4. 0·1011 g of the compound gave 0·1508 g CO_2 and 0·0771 g H_2O. By the Kjeldahl's method 0·708 g of the compound required 12 cm³ of N-H_2SO_4 for neutralization of ammonia. The original compound when boiled with NaOH evolved NH_3 and the dry residue when heated with soda lime gave a hydrocarbon containing 75% carbon. Deduce the formula of the compound.

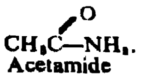
ANSWERS

A. (*b*) Four : $CH_2OH.CHOH.CHOH.CH_2OH$ 4. 75%.

C. 1.
$$\underset{\substack{\text{Isobutyramide}\\(A)}}{(CH_3)_2CHCONH_2} \xrightarrow[\text{alkali}]{Br_2+} \underset{\substack{\text{Isopropylamine}\\(B)}}{(CH_3)_2CHNH_2}$$

$$\xrightarrow[+HCl]{NaNO_2} \underset{\substack{\text{Isopropyl}\\\text{alcohol (C)}}}{(CH_3)_2CHOH} \xrightarrow{O} \underset{\substack{\text{Acetone}\\(D)}}{CH_3COCH_3}$$

$$CH_3.C{\equiv}CH \xrightarrow[H^+,Hg^{2+}]{H_2O} \underset{(D)}{CH_3COCH_3}$$

2. 
$CH_3C(=O){-}NH_2$.
Acetamide

3 A is $CH_3.CH_2.CH_2CONH_2$ *(Butanamide)*
B is $CH_3.CH_2.CH_2NH_2$ *(n-Propylamine)*
C is $CH_3.CH_2.CH_2.COONa$. *(Sodium butyrate)*
D is $CH_3.CH_2.CH_2.C{\equiv}N$ *(n-Propyl cyanide)*
E is $CH_3.CH_2.CH_2COOH$ *(n-Butyric acid)*
F is $CH_3.CH_2.CH_2OH$ *(1-Propanol)*
G is $CH_3.CH_2.CHO$ *(Propanal)*
H is $CH_3.CH_2.COOH$. *(Propionic acid)*

4. CH_3CONH_2 *(Acetamide)*

26

Esters, Oils and Fats

1. Esters and Esterification.—*An ester is produced when an alcohol reacts with an acid, organic or inorganic.* For example, ethyl acetate is the ester produced when ethyl alcohol reacts with acetic acid.

$$\underset{\text{Acetic acid}}{\mathrm{CH_3CO}}|\overline{\mathrm{OH+H}}|\underset{\substack{\text{Ethyl}\\\text{alcohol}}}{\mathrm{OC_2H_5}} \rightleftharpoons \underset{\substack{\text{Ethyl acetate}\\(\textit{Ester})}}{\mathrm{CH_3COOC_2H_5}}+\mathrm{H_2O}$$

Esters have characteristic fruity odour, *e.g.*, *amyl acetate* has an odour somewhat resembling that of bananas and amyl butyrate like that of apricot. Methyl butyrate has a fragrant smell that resembles pineapples. In fact presence of small quantities of this ester in ripe pineapples is responsible for its characteristic flavour and odour. Esters find use as artificial essence *for* flavouring and perfuming syrups, sweets and pastry.

The process of formation of ester that is not unlike neutralization is called **Esterification.** It is a reversible reaction and a dehydrating agent like sulphuric acid is used to absorb the water that is produced in the reaction above, thereby driving it towards the right.

During esterification, the —OH group of the acid is eliminated with H-atom of the alcohol as a molecule of water (*see* reaction between acetic acid and ethyl alcohol given above). With mineral acids such as hydrochloric acid (HCl), the reverse is the case.

$$\underset{\substack{\text{Ethanol}\\(\textit{Alcohol})}}{\mathrm{C_2H_5}}|\overline{\mathrm{OH+H}}|\underset{\substack{\text{Hydrochloric}\\\text{acid}\\(\textit{Mineral acid})}}{\mathrm{Cl}} \rightleftharpoons \underset{\substack{\text{Ethyl chloride}\\(\textit{Ester})}}{\mathrm{C_2H_5Cl}} + \mathrm{H_2O}$$

During neutralization, it is always the hydrogen of the acid that is eliminated with —OH group of the base as given below :

$$\underset{\substack{\text{Acetic acid}\\(\textit{Acid})}}{\mathrm{CH_3COO}}|\overline{\mathrm{H\ +\ HO}}\underset{\substack{\text{Sod. hydroxide}\\(\textit{Base})}}{\mathrm{Na}} \longrightarrow \underset{\substack{\text{Sodium acetate}\\(\textit{Salt})}}{\mathrm{CH_3COONa}} + \mathrm{H_2O}$$

Just as salts are metallic derivatives of acids, esters may be regarded as alkyl derivatives of acids obtained by replacing one or all the replaceable hydrogen atoms of the acid by alkyl groups. Nomenclature of esters is also similar to that for salts, the name of the metal radical in a salt is replaced by the name of the alkyl group present in the ester.

Acid	*Corresponding salt*	*Corresponding ester*
CH_3COOH Acetic acid	CH_3COONa Sodium acetate	$CH_3COOC_2H_5$ Ethyl acetate
C_2H_5COOH Propionic acid	C_2H_5COOK Potassium propionate	$C_2H_5COOCH_3$ Methyl propionate
H_2SO_4 Sulphuric acid	$KHSO_4$ Potassium hydrogen sulphate	$C_2H_5HSO_4$ Ethyl hydrogen sulphate
H_2SO_4 Sulphuric acid	Na_2SO_4 Sodium sulphate	$(CH_3)_2SO_4$ Methyl sulphate

2. **Distinction between Esters and Salts.**—Esterification, we have seen, is analogous to neutralization or salt formation. Esters are, therefore, regarded analogous to salts. This similarity between the two is, however, only supcrficial and they differ from one another in certain essential respects. The chief points of difference between them are summarized below :

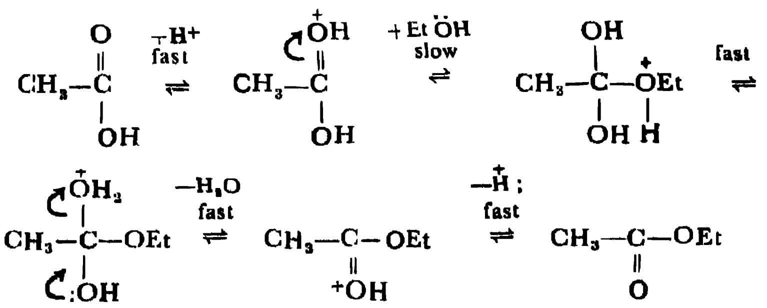
Esters	Salts
(*i*) Esters are covalent compounds only sparingly soluble in water and do not ionize.	(*i*) Salts are electrovalent compounds which are generally soluble in water and ionize in solution.
(*ii*) Esterification is a non-ionic reaction which proceeds slowly.	(*ii*) Salt formation is ionic and proceeds instantaneously.
(*iii*) They are readily hydrolysed to give the parent acid and alcohol.	(*iii*) Only salts of weak acids or bases undergo hydrolysis.
(*iv*) Esters are usually volatile, pleasant-smelling liquids.	(*iv*) Salts are generally non-volatile, odourless solids.
(*v*) Esters are neutral towards litmus.	(*v*) Salts may be neutral, acidic or basic towards litmus due to hydrolysis.

3. General Methods of Preparation of Esters.

(1) *By refluxing the acid with alcohol in the presence of small amounts of mineral acids as catalysts, e.g., 5-10% concentrated sulphuric acid*

$$RCO|\underline{OH\ +\ H}|OR' \xrightleftharpoons{H_2SO_4} RCOOR' + H_2O \qquad (\textit{v.g.})$$

Mechanism of the reaction is as follows :



Rate-determining step for esterification is addition of alcohol.

Alternatively, dry hydrogen chloride is passed into the acid alcohol mixture till there is 3% increase in weight and the mixture is refluxed.

Esterification may also be brought about by passing a mixture of the vapours of an acid and an alcohol over a metallic oxide catalyst (Thoria, ThO_2) at 575K.

(2) *By refluxing silver salt of an acid with an alkyl halide in ethanolic solution.*

$$\underset{\text{Silver acetate}}{CH_3COO|\boxed{Ag + I}}\,\underset{\text{Ethyl iodide}}{C_2H_5} \rightarrow \underset{\text{Ethyl acetate (Ester)}}{CH_3COOC_2H_5} + AgI \qquad (\textit{v.g.-ex.})$$

This method is very useful in cases where direct esterification is difficult, *e.g.*, tertiary alcohols.

(3) *By the action of an acid chloride or acid anhydride on an alcohol.*

$$\underset{\text{Acetyl chloride}}{CH_3CO|\boxed{Cl + H}}\,\underset{\text{Ethanol}}{|OC_2H_5} \rightarrow \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + HCl \qquad (\textit{v.g.-ex.})$$

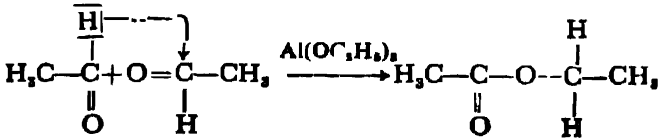
$$\underset{\text{Acid anhydride}}{(RCO)_2O} + \underset{\text{An alcohol}}{R'OH} \rightarrow \underset{\text{Ester}}{RCOOR'} + RCOOH \qquad (\textit{v.g.-ex.})$$

The reaction with tertiary alcohols is very slow. With acid anhydrides there is tendency for dehydration of alcohol to olefin With acid chlorides tertiary chlorides are also formed.

(4) *Methyl esters can very conveniently be obtained by treating an acid with an ethereal solution of diazomethane.*

$$\underset{\text{Acid}}{RCOOH} + \underset{\text{Diazomethane}}{CH_2N_2} \longrightarrow \underset{\text{Ester}}{RCOOCH_3} + N_2 \qquad (\textit{ex.})$$

(5) Ester may also be obtained *by condensation of aldehydes in presence of aluminium ethoxide* (**Tischenko reaction**).



$$\underset{\text{Acetaldehyde (Two molecules)}}{H_3C-\overset{H}{\underset{O}{C}}+O=\overset{}{\underset{H}{C}}-CH_3} \xrightarrow{Al(OC_2H_5)_3} \underset{\text{Ethyl acetate}}{H_3C-\underset{O}{C}-O-\overset{H}{\underset{H}{C}}-CH_3}$$

Acetaldehyde (*Two molecules*) Ethyl acetate

4. General Properties of Esters.—

(*a*) **Physical** : (*i*) Esters are colourless neutral liquids or solids with characteristic pleasant odours.

(*ii*) Boiling points of methyl and ethyl esters are lower than those of corresponding acids. Straight-chain esters have higher boiling points than their branched-chain isomers.

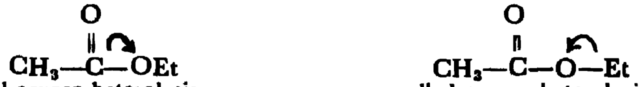
(*iii*) Esters with low molecular weight are fairly soluble in water. The solubility decreases as the molecular weight increases. All esters are soluble in most of the organic solvents. Many of them are good solvents for other substances.

(*b*) **Chemical** : (*i*) *Hydrolysis.* Esters are hydrolysed by acids or alkalis, to form alcohols and acids or their sodium salts. For example, ethyl acetate is hydrolysed as under :

$$\underset{\text{Ethyl acetate}}{CH_3CO|\boxed{OC_2H_5 + H}|OH} \xrightarrow{\text{Acid}} \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethanol}}{C_2H_5OH}$$

$$\underset{\text{Ethyl acetate}}{CH_3CO|\boxed{OC_2H_5 + H}|ONa} \longrightarrow \underset{\text{Sodium acetate}}{CH_3COONa} + \underset{\text{Ethanol}}{C_2H_5OH}$$

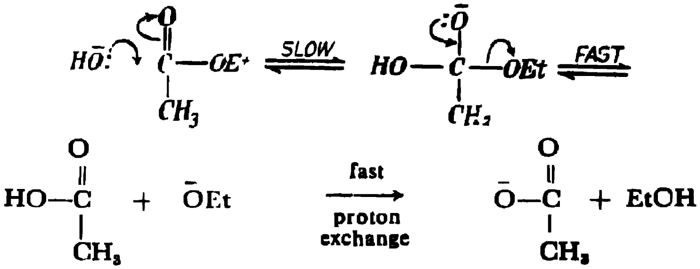
The hydrolysis of carboxylic esters may be represented in two ways :



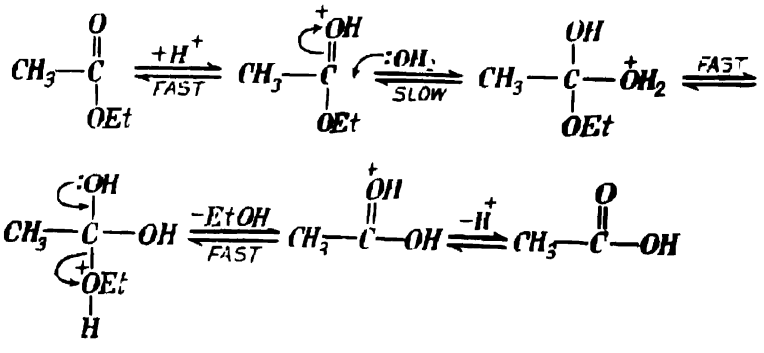
acyl-oxygen heterolysis alkyl-oxygen heterolysis

It has been found that alkaline hydrolysis proceeds with acyl-oxygen heterolysis and is a bimolecular reaction.

For example basic hydrolysis of ethyl acetate is formulated as under :



On the other hand acid hydrolysis proceeds with alkyl-oxygen heterolysis. This is also a bimolecular reaction and is formulated as under :



Rate determining step for acid hydrolysis is the addition of water.

During alkaline hydrolysis of an ester, sodium or potassium salt of the acid is obtained. *Since alkali salts of the higher fatty acids are soaps, alkaline hydrolysis of an ester is known as* **Saponification.** Saponification is more rapid than acid hydrolysis.

(*ii*) ***Reaction with Ammonia.*** Esters react with ammonia on heating to form amides. This reaction is an example of ***ammonolysis*** (***splitting by ammonia***).

$$CH_3CO|\overline{OC_2H_5 + H}|NH_2 \rightarrow CH_3CONH_2 + C_2H_5OH$$

Ethyl acetate Acetamide

(*iii*) ***Reaction with Phosphorus pentachloride.*** Phosphorus pentachloride reacts with esters to produce acid chloride and alkyl chlorides.

$$\underset{\text{Ethyl acetate}}{\overset{\text{Cl}}{CH_3CO}|{-}O{-}\overset{\text{PCl}_3|\text{Cl}}{|C_2H_5}} + PCl_5 \rightarrow \underset{\text{Acetyl chloride}}{CH_3COCl} + \underset{\text{Ethyl chloride}}{C_2H_5Cl} + POCl_3$$

(*iv*) ***Reduction.*** Reduction of an ester by means of excess of sodium and ethanol gives alcohols.

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + 4[H] \xrightarrow{C_2H_5OH/Na} \underset{\text{Ethanol}}{CH_3CH_2OH} + \underset{\text{Ethanol}}{C_2H_5OH}$$

$$RCOOR' + 4[H] \xrightarrow{C_2H_5OH/Na} RCH_2OH + R'OH \quad (g.)$$

Yield of RCH_2OH increases as the weight of alkyl radical R′ increases in the molecule of ester taken.

Other reducing agents used are : (*i*) lithium-aluminium hydride and (*ii*) hydrogen under pressure (100-300 atmospheres) in presence of copper chromate (*catalyst*) at 570K.

(*v*) *Alcoholysis* (*splitting by alcohol*). When an ester is refluxed with a large excess of alcohol in presence of a little acid (or sodium alkoxide (*catalyst*), the alcohol residue present is replaced by another a lower one).

$$\underset{\text{Butyl acetate}}{CH_3COOC_4H_9} + C_2H_5OH \overset{C_2H_5ONa}{\rightleftharpoons} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + C_4H_9OH$$

(*vi*) *Acidolysis* (*splitting by acid*). In acidolysis the acid residue present is replaced by another acid residue.

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + \underset{\text{Valeric acid}}{C_4H_9COOH} \rightleftharpoons \underset{\text{Ethyl valerate}}{C_4H_9COOC_2H_5} + \underset{\text{Acetic acid}}{CH_3COOH}$$

5. **Uses of Esters.**—Esters are used : (*i*) As solvents for cellulose, oils, gums, resins, etc., and as plasticisers.

(*ii*) In making artificial flavours and essences.

SOME INDIVIDUAL MEMBERS

6. **Ethyl Acetate, $CH_3COOC_2H_5$.**—It can be prepared by any one of the general methods for preparation of esters. It is, however, prepared in the laboratory by ***heating ethanol with glacial acetic acid in the presence of concentrated sulphuric acid or dry hydrogen chloride gas.***

$$CH_3CO\underline{OH + H}OC_2H_5 \overset{H_2SO_4}{\rightleftharpoons} CH_3COOC_2H_5 + H_2O$$

The acid acts as a protonating agent and serves to remove water as soon as it is formed and thus enables the reversible reaction to proceed to completion.

Expt. A distillation flask is fitted with a dropping funnel and a thermometer. It is connected to the condenser and a receiver as shown in Fig. 26·1. In the distillation flask are taken 50 ml of absolute alcohol with an equal volume of concentrated sulphuric acid. A mixture of 50 ml of absolute alcohol with an equal volume of glacial acetic acid is taken in the dropping funnel. The flask is heated to 413K in an oil bath and the mixture in the funnel is run in at the same rate at which the liquid distils over. The distillate consists of ethyl acetate contaminated with acetic acid, alcohol, water, a little of ether and sulphurous acid.

It is shaken with moderately strong sodium carbonate solution to remove acids. The upper oily layer of the ester is treated with a concentrated solution of sodium chloride or calcium chloride to remove the alcohol. It is now dried over fused calcium chloride and distilled. Ester distils over between 348-352K.

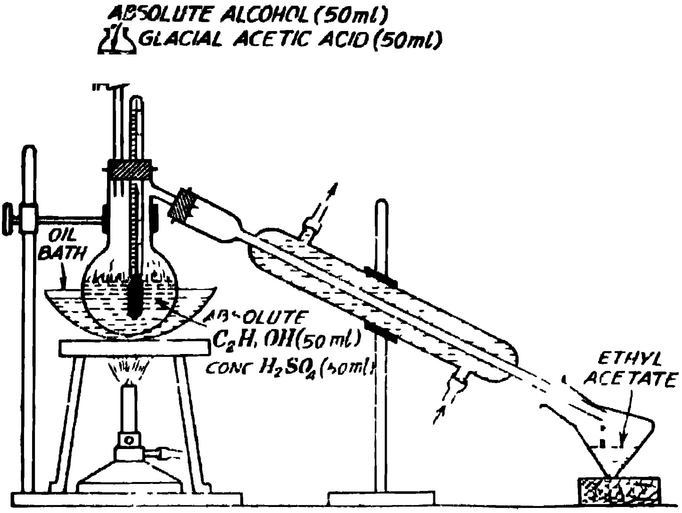


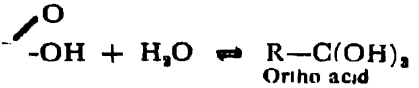
Fig. 26·1—Preparation of ethyl acetate.

Properties. Ethyl acetate is a colourless neutral liquid (b.p 350·5K ; Sp. Gr. 0·91) with a characteristic fruity odour. It is slightly soluble in water but completely miscible with alcohol and ether.

Chemically it is a typical ester and gives all the reactions discussed under general properties of esters.

Uses. Ethyl acetate is largely used as a solvent.

7. **Ethyl Orthoformate, $H.C(OC_2H_5)_3$.**—Ortho-esters have the general formula $R.C(OR')_3$ derived from the ortho-acids $R.C(OH)_3$. Ortho-acids have not yet been isolated but are possibly present in aqueous solution.

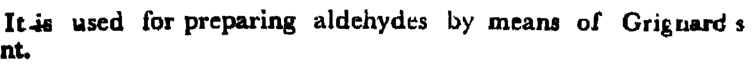


$$\overset{\diagup O}{\text{-}}OH + H_2O \rightleftharpoons \underset{\text{Ortho acid}}{R\text{—}C(OH)_3}$$

Ethyl orthoformate is an important ortho-ester. It can be prepared *by running ethanol and chloroform into sodium covered with ether.*

$$2CHCl_3 + 6C_2H_5OH + 6Na \rightarrow \underset{\text{Ethyl orthoformate}}{2H.C(OC_2H_5)_3} + 6NaCl + 3H_2$$

Ethyl orthoformate reacts with ketones to give ketals.



$$\begin{matrix}R\diagdown\\ \quad\rangle C{=}O\\ R'\diagup\end{matrix} + H.C(OC_2H_5)_3 \rightarrow \begin{matrix}R\diagdown\\ \quad\rangle C(OC_2H_5)_2\\ R'\diagup\end{matrix} + HCOOC_2H_5 \text{ (g}$$

It is used for preparing aldehydes by means of Grignard's reagent.

ESTERS OF INORGANIC ACIDS

8. Ethyl Hydrogen Sulphate, $C_2H_5HSO_4$.

Preparation. (*i*) Ethyl hydrogen sulphate is prepared by heating ethanol with an equal volume of concentrated sulphuric acid on a water-bath for about an hour.

$$\underset{\text{Ethanol}}{C_2H_5OH} + H_2SO_4 \rightleftharpoons \underset{\substack{\text{Ethyl hydrogen}\\\text{sulphate}}}{C_2H_5.HSO_4} + H_2O$$

The reaction mixture is treated with sufficient barium carbonate. Excess of the sulphuric acid is precipitated as barium sulphate and is filtered off. Barium salt of ethyl hydrogen sulphate left in the filtrate is decomposed with calculated quantity of dilute sulphuric acid and filtered. Ethyl alcohol and water present are removed by distillation under reduced pressure when ethyl hydrogen sulphate is obtained as a syrupy liquid.

(*ii*) By absorbing ethylene (from cracked petroleum) in concentrated sulphuric acid at 350-355K under pressure, ethyl hydrogen sulphate and ethyl sulphate are both obtained.

$$C_2H_4 + H_2SO_4 \longrightarrow \underset{\substack{\text{Ethyl hydrogen}\\\text{sulphate}}}{C_2H_5.HSO_4}$$

$$C_2H_5.HSO_4 + C_2H_4 \longrightarrow \underset{\text{Ethyl sulphate}}{(C_2H_5)_2SO_4}$$

Properties. Ethyl hydrogen sulphate is an oily liquid, sour in taste and having an acid reaction, *e.g.*, it decomposes carbonate. It is readily decomposed by boiling water, alcohol or concentrated sulphuric acid as given below :

$$C_2H_5\boxed{HSO_4 + H}OH \overset{\text{Hydrolysis}}{\rightleftharpoons} \underset{\text{Ethanol}}{C_2H_5OH} + H_2SO_4$$

$$\underset{\substack{\text{Ethyl hydrogen}\\\text{sulphate}}}{C_2H_5}\boxed{HSO_4 + H}\underset{\substack{\text{Ethanol}\\(excess)}}{OC_2H_5} \xrightarrow{410K} \underset{\text{Diethyl ether}}{C_2H_5.O.C_2H_5} + H_2SO_4$$

$$C_2H_5.HSO_4 \xrightarrow[\substack{H_2SO_4\\(excess)}]{430K} \underset{\text{Ethylene}}{C_2H_4} + H_2SO_4$$

When heated alone it gives diethyl sulphate,

$$2C_2H_5HSO_4 \longrightarrow (C_2H_5)_2SO_4 + H_2SO_4$$

9. Methyl Sulphate, $(CH_3)_2SO_4$.—This may be prepared :

(*i*) *By heating methyl iodide with silver sulphate.*

$$2CH_3I + Ag_2SO_4 \longrightarrow (CH_3)_2SO_4 + 2AgI$$

(*ii*) *By distilling under reduced pressure methyl hydrogen sulphate as obtained by heating methanol with concentrated sulphuric acid.*

$$CH_3OH + H_2SO_4 \longrightarrow CH_3HSO_4 + H_2O$$

$$2CH_3HSO_4 \longrightarrow (CH_3)_2SO_4 + H_2SO_4$$

(*iii*) *By the action of sulphur trioxide on methanol at low temperatures.*

$$2CH_3OH + 2SO_3 \longrightarrow (CH_3)_2SO_4 + H_2SO_4$$

The last two methods are used for the industrial preparation of methyl sulphate.

It is a colourless syrupy liquid (b.p. 461K) immiscible with water and poisonous in nature. It is used in the laboratory for the introduction of methyl radical in alcohols, phenols, and amines, *e.g.*,

$$\underset{\text{Methanol}}{CH_3OH}+(CH_3)_2SO_4 \longrightarrow \underset{\text{Dimethyl ether}}{CH_3.O.CH_3} + CH_3HSO_4$$

$$\underset{\text{Methylamine}}{CH_3NH_2}+(CH_3)_2SO_4 \longrightarrow \underset{\text{Dimethylamine}}{CH_3NHCH_3} + CH_3HSO_4$$

10. Ethyl Nitrate, $C_2H_5ONO_2$.—This may be prepared :

(*i*) *By heating ethyl iodide with silver nitrate in ethanol solution.*

$$C_2H_5\boxed{I + Ag}NO_3 \longrightarrow C_2H_5.O.NO_2+AgI$$

(*ii*) *By the action of nitric acid on alcohol in the presence of urea.*

$$C_2H_5O\boxed{H + HO}NO_2 \longrightarrow C_2H_5.O.NO_2+H_2O$$

Presence of urea removes any nitrous acid formed and thus prevents the violent oxidation of alcohol by nitric acid which occurs in the presence of nitrous acid.

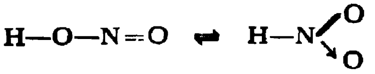
Ethyl nitrate is a colourless, pleasant-smelling liquid (b.p 633·5K). It is heavier than water and immiscible with it. When reduced with tin and hydrochloric acid, it produces ethanol and hydroxylamine, NH_2OH.

$$C_2H_5ONO_2+6[H] \longrightarrow C_2H_5OH+NH_2OH+H_2O$$

When boiled with water, it is hydrolysed to form ethyl alcohol and nitric acid.

$$\underset{\text{Ethyl nitrate}}{C_2H_5ONO_2}+HOH \longrightarrow \underset{\text{Ethanol}}{C_2H_5OH} + HONO_2$$

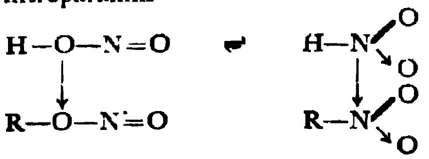
11. Esters of Nitrous Acid.—Nitrous acid exhibits tautomerism and occurs in two tautomeric forms as given below :



(*Trivalent nitrogen*) (*Pentavalent nitrogen*)

Here *tautomerism or dymeric isomerism* (*see* page 1·176) *is caused by the wanderings of a hydrogen atom between the polyvalent atoms, oxygen and nitrogen.*

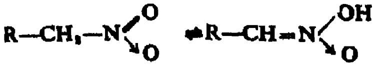
Corresponding to the isomeric forms of nitrous acid, we have two series of isomeric alkyl derivatives of nitrous acid, *viz.*, alkyl nitrites and nitroparaffins



Alkyl nitrite Nitroparaffin

To the Students. For some examples of tautomerism, *see*

$$\underset{\text{Hydrocyanic acid}}{H-C\equiv N} \rightleftharpoons \underset{\text{Isohydrocyanic acid}}{H-N\overset{\rightarrow}{=}C}$$ (*Page 1·176*)



Nitroalkane Isonitroalkane (*Page 1·171*)

12. Alkyl Nitrites, R.O.N.O.—The only important nitrites are ethyl and amyl nitrites. These are prepared by adding concentrated hydrochloric acid or sulphuric acid to aqueous sodium nitrite and the corresponding alcohol, *e.g.*,

$$C_2H_5O\boxed{H + HO}N{=}O \rightarrow C_2H_5ON{=}O + H_2O$$

Ethanol Ethyl nitrite

$$C_5H_{11}O\boxed{H + HO}N{=}O \rightarrow C_5H_{11}.O.N{=}O + H_2O \ (75\text{-}85\%)$$

Amyl alcohol Amyl nitrite

Ethyl nitrite (b.p. 290K) and amyl nitrite (b.p. 368K) are colourless, pleasant-smelling liquids. When treated with boiling water or dilute alkali, the esters are easily *hydrolysed.*

$$C_2H_5ONO + NaOH \rightarrow C_2H_5OH + NaNO_2$$

On *reduction* they yield hydroxylamine and alcohols.

$$C_2H_5O{-}N{=}O + 4[H] \rightarrow C_2H_5OH + NH_2OH$$

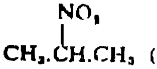
Ethyl nitrite Ethanol Hydroxylamine

Ethyl and amyl nitrites are used in medicine and as a means of preparing nitrous acid in anhydrous media, *e.g.*, by passing dry hydrogen chloride through an alcoholic solution of amyl nitrite, we get an alcoholic solution of nitrous acid.

13. Nitroalkanes or Nitroparaffins.—The nitroparaffins are named as the nitro derivatives of the corresponding paraffins, *e.g.*,

CH_3NO_2 (nitromethane)

$C_2H_5NO_2$ (nitroethane)



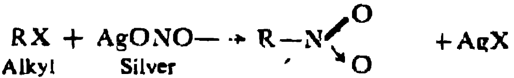
$$CH_3.\overset{NO_2}{\underset{|}{C}}H.CH_3$$

(2-nitropropane)

Nitroalkanes are termed primary, secondary and tertiary depending upon the nature of carbon atom (primary, secondary or tertiary) with which nitro group is attached.

RCH_2NO_2	R_2CHNO_2	R_3CNO_2
Primary	Secondary	Tertiary

Preparation. (*i*) *By heating an alkyl halide with silver nitrite in aqueous ethanolic solution.*



Alkyl halide Silver nitrite Nitroparaffin

The yield is good for lower nitroparaffins. Some alkyl nitrite is also obtained and its proportion increases with the length of the carbon chain. The mixture can, however, be readily separated by fractional distillation since an alkyl nitrite has a much lower boiling point than the isomeric nitroparaffin. For example, boiling point of ethyl nitrite is 290K while nitroethane boils at 388K.

(*ii*) *By boiling an aqueous solution of sodium nitrite with a halogenocarboxylic acid.* Nitro-acid first formed readily loses carbon dioxide to yield the nitroparaffin.

$$CH_2Cl.COOH \xrightarrow{NaNO_2} CH_2(NO_2)COOH \xrightarrow{-CO_2} CH_3.NO_2[35\text{-}3[illegible]\%)$$

Chloroacetic acid Nitroacetic acid

(*iii*) *By direct nitration of paraffins.*

$$R\boxed{H + HO}NO_2 \rightarrow RNO_2 + H_2O$$

The paraffin is heated with nitric acid (or with oxide of nitrogen) at 425-750K, each paraffin has its own optimum temperature (*vapour phase nitration*).

(*iv*) *By hydrolysis of α-Nitro-olefins.* A recent method for the preparation of nitro-paraffins is the hydrolysis of α-nitro-olefins with water, acid or alkali.

$$(CH_3)_2C{=}CH.NO_2+H_2O \rightarrow (CH_3)_2CO+CH_3NO_2$$

2-methyl-1-nitro-1-propene Acetone Nitro-methane

Properties : Physical. Nitroparaffins are colourless (when pure), pleasant-smelling liquids sparingly soluble in water. Most of them can be distilled without decomposition under atmospheric pressure.

Chemical. (*i*) *Reduction.* Nitroparaffins, when reduced in acid solution, yield primary amines. Lithium aluminium hydride also gives these products.

$$RNO_2 \ + \ 6[H] \xrightarrow{\text{metal/acid}} RNH_2 \ + \ 2H_2O$$

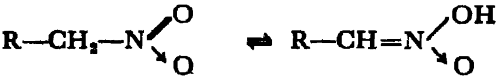
Nitroparaffin Primary amine

Catalytic reduction also produces primary amines. Yield with Raney nickel (*catalyst*) is 90-100%. Reduction in neutral solution (with zinc dust and ammonium chloride) yields hydroxylamine derivative.

$$RNO_2+4[H] \xrightarrow{Zn/NH_4Cl} R.NHOH \ + \ H_2O$$

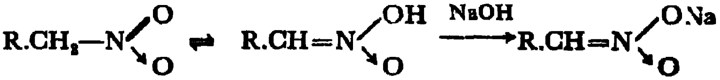
Hydroxylamine derivative

(*ii*) *Pseudo-acid Character.* Primary and secondary nitro-compounds (those containing α-hydrogen atoms) exhibit tautomerism as given below :



Pseudo-acid form *Aci*-form or *Nitronic acid*

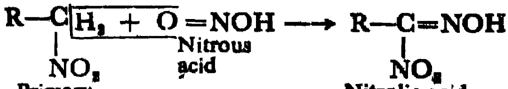
The nitronic acids do not dissolve in aqueous sodium carbonate but are soluble in sodium hydroxide solution.



Nitroparaffin Isonitroparaffin Sodium salt

Thus, sodium hydroxide shifts the equilibrium to the right. The nitro compounds, which behave as acids in the presence of strong alkalis but not in their absence, are called **pseudo-acids.**

(*iii*) *Action of Nitrous acid.* Primary nitro-compounds react with nitrous acid to form crystalline nitrolic acids which dissolve in alkali to give red solution.

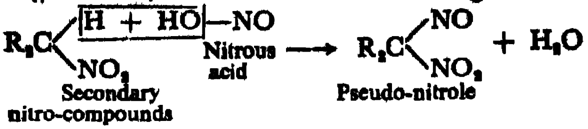


$$R-\underset{NO_2}{\underset{|}{C}}\boxed{H_2 \ + \ O}{=}NOH \longrightarrow R-\underset{NO_2}{\underset{|}{C}}{=}NOH$$

Nitrous acid

Primary nitro-compound Nitrolic acid

Secondary nitro-compounds give colourless crystalline *pseudo-nitroles* (ψ-nitroles) which dissolve in alkali to give blue solution.



(*iv*) ***Hydrolysis.*** Primary nitro-paraffins are hydrolysed by boiling with hydrochloric acid or 85% sulphuric acid to give hydroxylamine and carboxylic acid.

$$RCH_2.NO_2 + H_2O \xrightarrow{HCl} RCOOH + NH_2OH$$

This reaction is being used for the manufacture of hydroxylamine.

Secondary nitro-paraffins on hydrolysis yield ketones and nitrous oxide.

$$\underset{\substack{\text{Secondary}\\\text{nitro-paraffin}}}{2R_2CH.NO_2} \xrightarrow{HCl} \underset{\text{Ketone}}{2R_2CO} + N_2O + H_2O$$

Tertiary nitro-paraffin remains unaffected.

(*v*) *Halogenation.* Primary and secondary nitro-paraffins are readily halogenated in alkali solution. The halogen atom enters α-position.

Primary give both mono- and di-halogeno derivatives, whereas secondary give only monohalogeno derivative. Nitromethane is exceptional and gives trihalogeno derivatives.

$$CH_3NO_2 + 3Cl_2 + 3NaOH \longrightarrow \underset{\text{Chloropicrin}}{CCl_3.NO_2} + 3NaCl + 3H_2O$$

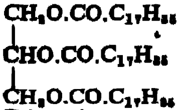
Uses. Nitroalkanes are less toxic and not much inflammable. Hence these are being widely used as solvents for fats, oils, shellac-cellulose derivatives and rubber.

14. Distinguishing Properties of Nitroparaffins and Alkyl Nitrites.—A nitro-paraffin can be distinguished from its isomeric alkyl nitrite as summarized in the table below :

Property	*Alkyl nitrite*	*Nitro-paraffin*
1. Boiling point.	Low.	Much higher.
2. Reduction with metal and acid.	Yields Alcohol+hydroxylamine or ammonia. (*See* page 2·288)	Gives corresponding primary amine. (*See* page 2·289)
3. With alkalis.	Readily hydrolysed giving alkali nitrite and corresponding alcohol. (*See* page 2·288)	Not decomposed ; may form soluble sodium salt. (*See* page 2·289)
4. Action with Nitrous acid.	No action.	Primary yields nitrolic acid : Secondary reacts to give pseudo-nitrole. (*See* page 2·289)

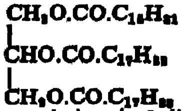
15. Oils and Fats.—Oils and fats are glyceryl esters or glycerides of higher fatty acids. *Those which are liquids at ordinary tem-*

peratures are called **Oils.** These contain a larger proportion of unsaturated acids than do fats *which are solids at ordinary temperatures.* The common simple glycerides (when all acids are the same) are tristearin, tripalmitin and triolein (*see* page 2·157). Mixed glycerides (when the acids are different) are, however, definitely more common.



$$\begin{array}{l} CH_2O.CO.C_{17}H_{35} \\ | \\ CHO.CO.C_{17}H_{35} \\ | \\ CH_2O.CO.C_{17}H_{35} \end{array}$$

Tristearin
(*Simple glyceride*)



$$\begin{array}{l} CH_2O.CO.C_{15}H_{31} \\ | \\ CHO.CO.C_{17}H_{33} \\ | \\ CH_2O.CO.C_{17}H_{33} \end{array}$$

α-palmito-α' : β-diolein
(*Mixed glyceride*)

Oils and fats may be of animal or vegetable origin, *e.g.*, whale oil (an oil) and tallow (a fat) have an animal origin while linseed oil (an oil) and coconut oil (a fat) have vegetable origin. *They differ from mineral oils and essential oils.*

Mineral oils *have a mineral origin and are a mixture of hydrocarbons.* Kerosene is a mineral oil.

Essential oils *are found in various plants. These are highly volatile, pleasant-smelling liquids.* Clove oil, lemon oil and turpentine are examples of essential oils.

Common methods employed for the extraction of oils and fats are :

(*i*) *Melting.* Animal fats are generally separated from animal tissue by heating when the fat melts and flows down.

(*ii*) *Crushing.* Vegetable oils, *e.g.*, cottonseed oil, groundnut oil, are extracted from oilseeds by crushing followed by pressing in a hydraulic press. The residue called oilcake is used as cattle feed.

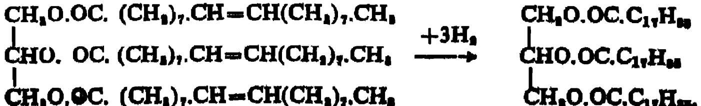
(*iii*) *Extraction with Solvents.* Fats and oils being soluble in organic solvents, *e.g.*, petroleum ether, are more carefully extracted by means of these.

16. Properties and Uses of Oils and Fats.

Properties : Physical. When pure, these are colourless, odourless, neutral liquids or solids. They are lighter than water and immiscible with it but dissolve in organic solvents, *e.g.*, ether and benzene. When agitated with water in the presence of soap, gelatin, etc. (*emulsifiers*) they form emulsions.

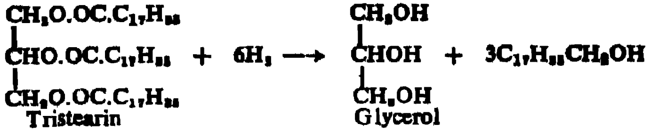
Chemical. (*i*) *Hydrolysis.* Oils and fats are hydrolysed when heated with water alone or in the presence of acids and yield glycerol and higher fatty acids. With alkalis they give glycerol and soap (*see* page 2·157).

(*ii*) *Hydrogenation.* Oils are glycerides of unsaturated fatty acids. These are changed to solid fats when hydrogen gas is passed into them under pressure and in the presence of finely-divided nickel (*catalyst*). The unsaturated acid radicals change into saturated ones as a result of hydrogenation. For example,



$$\begin{array}{l} CH_2O.OC.\,(CH_2)_7.CH{=}CH(CH_2)_7.CH_3 \\ | \\ CHO.\,OC.\,(CH_2)_7.CH{=}CH(CH_2)_7.CH_3 \\ | \\ CH_2O.OC.\,(CH_2)_7.CH{=}CH(CH_2)_7.CH_3 \end{array} \xrightarrow{+3H_2} \begin{array}{l} CH_2O.OC.C_{17}H_{35} \\ | \\ CHO.OC.C_{17}H_{35} \\ | \\ CH_2O.OC.C_{17}H_{35} \end{array}$$

Triolein (m.p. 256K) Tristearin (m.p. 333K) (*iii*) *Hydrogenolysis.* On passing excess of hydrogen through an oil or fat, it yields glycerol and a higher alcohol. For example,



$$\begin{array}{l} CH_2O.OC.C_{17}H_{35} \\ | \\ CHO.OC.C_{17}H_{35} \\ | \\ CH_2O.OC.C_{17}H_{35} \\ \text{Tristearin} \end{array} + 6H_2 \longrightarrow \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \\ \text{Glycerol} \end{array} + 3C_{17}H_{35}CH_2OH$$

This splitting up of the fat molecule by hydrogen is called *hydrogenolysis.*

(*iv*) *Drying.* Certain oils like linseed oil change into hard solids on exposure to air. These are called **Drying oils** and find use in paint and varnish[*] industry. Drying is catalysed by litharge and various other metallic oxides. Some other oils like cottonseed oil thicken slowly and contain a smaller percentage of the glycerides of unsaturated acids than the drying oils. These are called **semi-drying oils.**

Drying involves oxidation, polymerization and colloidal gel formation. The mechanism of the process is, however, complicated and not definitely known.

(*v*) *Rancidification.* The unpleasant smell which fats and oils develop on long exposure to moist air is due to *rancidity.* This results from partial saponification (*hydrolysis*) which sets free strongly smelling fatty acids.

For example, butter on hydrolysis yields volatile fatty acids having unpleasant odour.

Another form of rancidity is due to oxidation of unsaturated fats promoted by heat and light. The oxidation yields aldehydes and acids which have a strong smell.

Uses. These are largely used (*i*) as articles of food, (*ii*) for toilet purposes, (*iii*) in medicine, (*iv*) as lubricants, (*v*) as illuminants, and (*vi*) in the manufacture of soap, glycerine and paints.

17. Hydrogenation of Oils.—Most of the housewives prefer solid fats to liquid oils for cooking purposes. Accordingly, millions of kilograms of groundnut oil or cottonseed oil are changed to solid edible fat (*vegetable ghee*) each year by hydrogenation in presence of a suitable catalyst. Hydrogenation converts only a part of the glycerides of unsaturated acids into those of saturated acids. Different steps involved in the actual manufacture of vegetable ghee are :

(*i*) *Removal of Free Acids.* The oil is warmed in a pan and treated with a calculated quantity of sodium hydroxide to neutralize the free fatty acids. The salts formed as a result of neutralization come up in the form of a scum along with some of the suspended matter.

---

[*] Paints are mixtures of linseed oil and some suitable pigment. Before applying turpentine is added as a *thinner* which enables us in applying a thin and uniform coating. On standing turpentine evaporates quickly while linseed oil dries in a few days leaving a hard and water-proof coating.

Varnishes are mixtures of linseed oil and a resin dissolved in some suitable solvent. The resin gives a gloss to the hard films obtained as a result of the drying of the oil.

Lacquer is a varnish to which some pigment has been added.

(*ii*) ***Bleaching.*** The oil from the first tank is decanted into the second and treated with animal charcoal at 353K or so. The colouring matter is adsorbed by animal charcoal and the oil is filtered.

(*iii*) *Deodorising.* The bleached oil is treated with superheated steam for deodorising.

(*iv*) *Hydrogenation or hardening of oil.* The oil purified above is taken in an iron tank surrounded by a heating jacket at 423-473K. Some finely divided nickel is suspended in the oil and hydrogen gas is passed in under pressure. Finely divided nickel acts as a catalyst in hydrogenation.

The hydrogenation is continued until a fat of the desired consistency is obtained. The hardened oil is taken out and freed from the catalyst by filtration. Some flavouring material somewhat resembling genuine ghee is then added to this before placing it on the market.

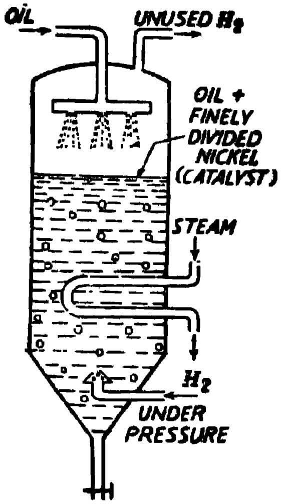


Fig. 26·2—Hydrogenation of oils.

18. Analysis of Oils and Fats.—The composition and purity of a given fat is determined by means of a number of physical and chemical tests. Various physical tests are the determination of its physical constants such as melting point, specific gravity and refractive index. Various chemical tests which give an indication of the type of fatty acids present in the fat or oil are :

(*i*) **Acid Value.** *It is the number of milligrams of potassium hydroxide required to neutralize 1 g of the fat or oil.* The acid value indicates the amount of the free acid present in the fat or oil.

To determine acid value, a weighed quantity of the fat is dissolved in alcohol and titrated against a standard alkali using phenolphthalein as indicator.

(*ii*) **Saponification Value.** It is the number of milligrams of potassium hydroxide required to neutralize the fatty acids resulting from the complete hydrolysis of 1 g of the oil or fat.

To determine the saponification value, a weighed quantity of the given fat is refluxed with a known volume of standard alcoholic potash solution. The unused alkali is then titrated against some standard acid. Saponification values of some common oils are :

Coconut oil = about 250
Olive oil = ,, 200

(*iii*) **Iodine Value.** *It is the number of grams of iodine which combine with 100 grams of oil or fat.* It indicates the degree of unsaturation of acids in the fat or oil.

In *Hubl's method* of determination of the iodine value, a known weight of oil or fat is dissolved in carbon tetrachloride and treated with a known volume of standard solution of iodine and mercuric chloride in ethanol. The unused iodine is titrated against a standard thiosulphate solution.

Iodine values of some common oils are :

Coconut oil = 10 ; Olive oil = 88 ; Linseed oil = 108.

(*iv*) **Reichert-Meissl Value (R/M Value).** *It is the number of millilitres of 0·1 N potassium hydroxide solution required to neutralize the distillate of 5 g of hydrolysed fat.* It represents the amount of steam volatile fatty acids present in the oil or fat.

5 g of the fat is hydrolysed with sodium hydroxide and the mixture is acidified with dilute sulphuric acid and steam distilled when acids with carbon content up to 10 being volatile in steam distil over. The distillate is cooled and filtered and titrated against 0·1 N-alkali.

Reichert-Meissl values of some common fats and oils are :

Butter=20 ; Coconut oil=80 ; Cottonseed oil=Less than 1.

19. Classification of Oils.—On the basis of iodine value the oils have been sub-divided into following three groups :

(*a*) *Drying oils*. These are oils with iodine values above 120. They harden slowly on exposure to air to form resinous solid. These are glycerides of highly unsaturated acids, *e.g.*, linoleic and linolenic acid. Linseed oil is a typical drying oil and consists of : Linolenic acid ester (80%), Linoleic acid ester (15%) and Triolein (5%).

Tung oil (China-wood oil) is another example of an excellent drying oil.

Drying oils find use in paints and in the manufacture of oil cloth, rexin and *linoleum* (*mixture of ground cork and boiled linseed oil rolled into sheet which hardens on standing*).

(*b*) *Semi-drying oils*. These are oils with iodine values 90 to 120. They thicken very slowly when exposed to air. Cottonseed oil and sesame oil are examples of semi-drying oils.

(*c*) *Non-drying oils*. These have iodine values less than 90. They do not thicken when exposed to air. They consist of mainly triolein. Some examples of this class are olive oil, coconut oil and castor oil.

20. Distinction between Animal and Vegetable Fats.—Animal fats contain cholesterol—an unsaturated alcohol, with molecular formula $C_{27}H_{46}O$. Cholesterol forms rhombic plates (m.p. 421K).

Vegetable fats contain phytosterol which crystallizes as needles (m.p. 405-417K). This makes the distinction between animal and vegetable fats possible.

21. Waxes.—These are also esters of higher fatty acids. They, however, differ from oils and fats which are glycerides of higher fatty acids in being esters of higher homologues of monohydric alcohols, *e.g.*,

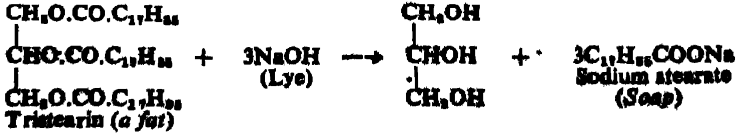
Name	*Chemical name*	*Formula*
Beeswax	Myricyl palmitate	$C_{15}H_{31}COOC_{30}H_{61}$
Spermaceti	Cetyl palmitate	$C_{15}H_{31}COOC_{16}H_{33}$
Carnauba wax	Myricyl cerotate	$C_{25}H_{51}COOC_{30}H_{61}$

Paraffin wax (a petroleum product) is, however, a mixture of higher hydrocarbons and thus is entirely different from natural waxes.

Waxes are used in the manufacture of boot polishes, furniture polishes and varnishes.

SOAP AND SOAPLESS DETERGENTS

22. Saponification or Soap-making.—Common soaps are sodium or potassium salts of higher fatty acids, *e.g.*, stearic, palmitic and oleic acids. The sodium salts are termed *hard soap* whereas the potassium salts give *soft soap*. These are obtained from oils and fats, *e.g.*, *tristearin* is obtained from beef and mutton tallow, tripalmitin is present in palm oil and triolein is found in lard, olive oil and cottonseed oil. In India soap is generally manufactured from coconut oil, groundnut oil, *til oil* and *mahua oil*. If we treat tristearin with sodium hydroxide solution called *lye*, they react to form soap and glycerine. The process is called *saponification*.



$$\begin{array}{l} CH_2O.CO.C_{17}H_{35} \\ | \\ CHO.CO.C_{17}H_{35} \\ | \\ CH_2O.CO.C_{17}H_{35} \\ \text{Tristearin } (\textit{a fat}) \end{array} + \underset{\text{(Lye)}}{3NaOH} \longrightarrow \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + \underset{\substack{\text{Sodium stearate} \\ (\textit{Soap})}}{3C_{17}H_{35}COONa}$$

23. Manufacture of Soap.—Two processes generally employed for the manufacture of soap are :

(1) **The Hot Process.** Different steps involved in the manufacture of soap by hot process are :

(*i*) *Saponification.* The oil or fat is taken in a giant iron-pan (*Soap kettle*) and heated with open steam. The alkali solution—10 per cent caustic soda solution (*lye*)—is added in thin stream while steam keeps the mass boiling and also ensures thorough mixing. After several hours the saponification is complete and a frothy mixture of sodium salts (*soap*) and glycerine is obtained.

$$\textit{Fat or Oil} + \textit{Lye} \longrightarrow \textit{Soap} + \textit{Glycerol}$$

(*ii*) *Salting out of soap.* Slight excess of the alkali in the transparent reaction mixture indicates that saponification is complete. Common salt or brine is now added to precipitate soap and heating is continued. After some hours soap forms the upper layer as granular mass. *This is called salting out of soap.*

The lower layer consisting of glycerol, salts and unused alkali solution (*spent lye or sweet lye*) is drawn from below and used for the recovery of glycerol (*see* page 2·157).

(*iii*) *Finishing.* The soap so obtained is boiled again with caustic soda for complete saponification of any unsaponified fat and the spent lye again drawn off. The solid soap is next boiled with water to dissolve out the excess alkali and allowed to settle when the impure soap called *nigre* forms the lower layer. The upper layer of pure soap is transferred through a *swing pipe* to a steam-jacketed tank called *crutcher.*

Here it is shredded into small chips, dried to the requisite moisture content and mixed with colouring matter and perfumes. In the case of laundry soap some fillers, *e.g.*, rosin, sodium silicate, borax and sodium carbonate, are also added. These have some detergent value and are cheaper than soap.

It is next run into moulds and permitted to solidify. The bigger blocks are cut into slabs by means of steel wires. The slabs are finally cut into cakes of desired size and stamped.

(2) **The Cold Process.** The oil or the molten fat is taken in an iron pan fitted with a stirrer and treated there with caustic soda solution (*Lye*). The charge is stirred until the soap begins to set. It is solidified in frames and cut into slabs as given above. All the glycerine set free remains in the soap. Usually starch or some other filling material is thoroughly mixed with the oil previous to the addition of caustic soda. The usual proportions of the various ingredients are : alkali (1 part), water (7 parts) and starch (1 part). The process is, however, not so economical as the hot process and does not yield pure stuff. The hot process is, therefore, decidedly superior to this.

(3) **Modern Process.** In the processes recently developed, the fat is hydrolysed with hot water under pressure in the presence of catalyst, *e.g.*, lime or zinc oxide (*Ittner Process*), or dilute sulphuric acid and aromatic sulphonic acids (*Twitchel Process*). The free acid,

obtained as a result of hydrolysis, is neutralized with caustic soda or sodium carbonate. The methods are cheaper and simpler.

Large-scale apparatus built for continuous hydrolysis of fats consists of a tower about 65 feet high. Fat is introduced into the tower at the bottom while hot water at about 523K enters at the top. Fat rises up through water and gets hydrolysed in the presence of a catalyst which is also added.

Fatty acids from the top of the tower are neutralized to soap in a continuous process. Dilute glycerol leaving the bottom of the tower is used for recovery of glycerol.

24. How does Toilet soap differ from Laundry soap ?—Toilet soaps are manufactured from the best quality fat or oils. Great care is taken to add just the right amount of lye to see that there is no free alkali, injurious to skin, in the finished product. Laundry soaps are obtained from cheaper fats and oils. All soaps contain some perfume to conceal the unpleasant smell of raw soap but expensive perfumes are added to toilet soaps to make them pleasant smelling. Toilet soaps contain no filling materials usually present in laundry soap.

25. Some Special Varieties of Soap.—There are many kinds of soap in the market, *e.g.*, *floating soaps* made by beating large quantities of air into soap in a crutcher while it is in the creamy stage. *Transparent soap* may contain glycerol or alcohol and may be obtained by dissolving soap in alcohol and evaporating the solvent alcohol. *Medicated soaps* contain some substances of medicinal value added to them, *e.g.*, *neem* soap, carbolic soap. *Shaving soaps* are potassium sodium stearates (which produce lasting lather) containing gum and glycerine to prevent rapid drying of lather.

26. Cleaning Action of Soap.—A soap has two dissimilar ends. At one end is the hydrocarbon chain which is non-polar and oil-soluble (lyophilic or lipophilic). The other is the carboxylate salt end which is polar and water-soluble (hydrophilic).

$$C_{17}H_{35}-CO\overset{-}{O}\overset{+}{Na}$$

Non-polar Polar
lyophilic hydrophilic
Sodium stearate—a soap

When soap is added to water, its molecules make a unimolecular film on the surface of water with their carboxyl groups dissolved in water and the hydrocarbon chains standing on end to form a hydrocarbon layer.

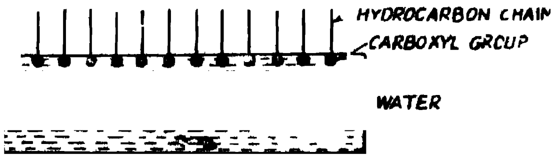


Fig. 26·3—Unimolecular film of soap molecules on water surface.

When a cloth with spot of dirt is soaked with soap solution, soap dissolves dirt (fat or oil with dust etc. adsorbed in it) by forming *miscelles* in which oil or fat is at the centre of the sphere with fat-soluble hydrocarbon chains of soap dissolved in it. The water-soluble carboxylate ions make a hydrophilic surface around this sphere and render the entire miscelles of oil or fat water-soluble. Thus the miscelles dissolves in water and is washed away.

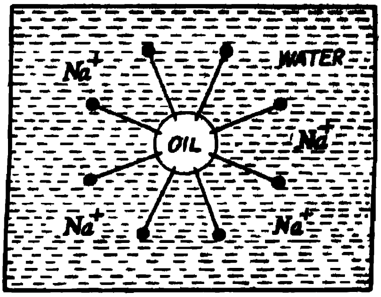


Fig. 26·4—Oil miscelles with hydrocarbon chains of soap dissolved in it. Water-soluble carboxylate ions render the entire miscelles water-soluble.

We find tnat soap tends to concentrate on the surface of solution and, therefore, lowers its surface tension and thus causes foaming. This helps it to penetrate the fabric. It emulsifies fat in dirt forming a miscelles and renders the entire miscelles water-soluble. The dirt is thus washed away by water.

27. **Synthetic Detergents.**—Development of synthetic detergents is a big achievement in the field of cleansing. These possess the desirable properties of ordinary soaps and can be used with hard water and also in acidic solutions. These are salts of sulphonic acids or alkyl hydrogen sulphates in comparison to soap which are salts of carboxylic acids. Their calcium or magnesium salts are soluble in water.

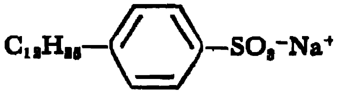
Their oil-soluble (lyophilic) part is the hydrocarbon chain and the water soluble part may be : (*i*) An anionic group such as sulphate or sulphonate. (*ii*) A cationic group, *e.g.*, amine salt or quaternary ammonium compound. (*iii*) It may also be a non-ionic group such as alcohol or ether. A few typical detergents are given below :

(*a*) *Alkyl sulphates* (*anionic*) *e.g.*,

(*i*) $CH_3—(CH_2)_{10}—CH_2OSO_3^-Na^+$
Sodium lauryl sulphate

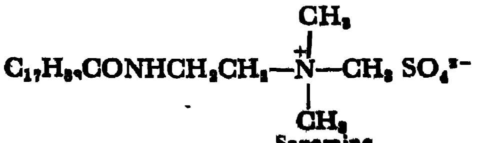
(*ii*) $CH_3—(CH_2)_{16}—CH_2OSO_3^-Na^+$
Sodium stearyl sulphate

(*b*) *Alkyl benzenesulphonates* (*anionic*), *e.g.*,



Sodium dodecylbenzenesulphonate (SDS)

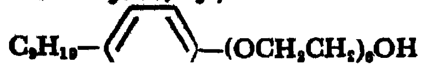
(*c*) *Cationic detergents, e.g.*,



$$C_{17}H_{33}CONHCH_2CH_2—\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{\overset{+}{N}}}—CH_3\ SO_4^{2-}$$

Sapamine

(*d*) *Non-ionic detergents, e.g.*,



Ethoxylate nonylphenol

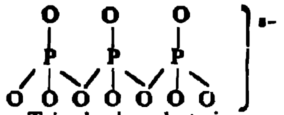
Synthetic detergents have wonderful properties but some of them have very low biodegradability. They are resistant to bacterial attack and are not fully degraded in sewage treatment plants. Their *discharge into rivers causes a serious pollution problem.*

These are wetting agents which lower the surface tension of water and act as cleansing agent as explained above in the case of soap. These can be used for delicate fabrics as they do not hydrolyse to give hydroxyl ions and work equally well with hard and soft water.

What does your Detergent contain ?—Your synthetic detergent contains little of real detergent. Its various constituents are :

Sodium alkylbenzenesuphonate	18%
Dedusting agent	3%
Foam booster	3%
Sodium tripolyphosphate, *builder*	50%
Anti-corrosion agent	6%
Optical brightener	0·3%
Water and inorganic filler	19·7%

Function of tripolyphosphate is to produce OH^- ion (by reacting with water) and keep the wash water slightly alkaline, thus helping to emulsify grease particles.



$$+ 2H_2O \rightarrow HP_2O_7^{3-} + H_2PO_4^- + OH^-$$

Tripolyphosphate ion

Tripolyphosphate ion can also tie up Ca^{2+} and Mg^{2+} ions which cause hardness of water.

28. Candles.—Mixture of fatty acids obtained by hydrolysis of fats with superheated steam is heated to 333K and pressed when liquid acids are separated. The solid cake obtained is known as '*stearin*' and is mainly a mixture of stearic and palmitic acids. Stearin is mixed with about 90% paraffin wax and melted. The molten mass is poured into metal tubes each carrying a cotton thread stretched along its axis. On cooling the mixture solidifies and candles are obtained.

QUESTIONS

Essay Type

1. Describe the preparation and properties of Ethyl acetate. (*Punjabi B.Sc. 1976*)

2. Define Esterification with an example and describe its mechanism. How will you obtain (*i*) Ethyl alcohol, (*ii*) Acetic acid, (*iii*) Acetyl chloride and (*iv*) Acetamide from ethyl acetate ? (*Guru Nanak Dev B.Sc. 1977*)

3. How would you prepare nitro-paraffins ? How will you distinguish between an alkyl nitrite and a nitro-alkane ? Explain the reactions with equations. (*Indore B.Sc. 1967 ; Agra 1965 Supp*)

4. Describe the preparation and uses of dimethyl sulphate. (*Kerala B.Sc. 1975*)

5. What is the chemical character of fat ? Explain the difference between oils, fats and waxes. What are their industrial uses ? (*Jabalpur B.Sc. 1976*)

6. What is the chemical character of a fat ? Explain the difference between oils, fats and waxes. Distinguish between mineral, vegetable and essential oils. (*Lucknow B.Sc. 1967 ; Allahabad 1966 ; Gorakhpur 1967 ; Nagpur 1965*)

7. What are oils and fats ? Define the various oil constants and state their significance in evaluating the quality of an oil. Give their industrial uses.
(*Jodhpur B.Sc. 1965 ; Kashmir 1960 ; Agra 1960 Supp.*)

8. Write explanatory notes on : (*a*) Saponification value, (*b*) Iodine value, and (*c*) Hardening of oils. (*Lucknow B.Sc. 1965 ; Kashmir 1960*)

9. Give briefly the manufacture of soap.
(*Lucknow B.Sc. 1967 ; Allahabad 1966 ; Gorakhpur 1967*)

10. What are oils, fats and soap ? Describe how vegetable ghee is manufactured starting from oilseeds. (*Guru Nanak Dev B.Sc. 1971*)

Short Answer Type :

1. How can nitroalkanes be distinguished from alkyl nitrites ?
(*Delhi B.Sc. 1976 Supp.*)

2. Why are primary nitroalkanes acidic in nature ? (*Delhi B.Sc. 1976*)

3. What are oils, fats and soap ? (*Guru Nanak Dev B.Sc. 1971*)

4. How does soap solution remove dirt particles from cloth ?
(*Guru Nanak Dev B.Sc. 1971*)

5. Sketch the structural formulae of (*i*) Ethylacetate and (*ii*) Methyl propionate. (*Guru Nanak Dev B.Sc. 1977*)

6. How do you explain the formation of ethyl nitrite and nitroethane when ethyl bromide reacts with potassium nitrite and silver nitrite respectively ?

7. What are drying oils ?

8. Give electronic mechanism of Esterification.
(*Kerala B.Sc. 1975 ; Delhi 1976*)

9. Define the saponification value of a fat and explain its significance.
(*Madurai B.Sc. 1976 October*)

10. How was it established that esterification involves the cleavage of the O—H bond of the alcohol and C—OH bond of the acid ?
(*Delhi B.Sc. Hons. 1977*)

11. Nitromethane dissolves in alkali. Explain why. (*Andhra B.Sc. 1978*)

12. Nitromethane slowly dissolves in aqueous alkali but methane does not do so. Explain. (*Madras B.Sc. 1978*)

13. Compare the behaviour of primary, secondary and tertiary nitroalkanes towards nitrous acid. (*Madras B.Sc. 1978*)

14. Discuss the mechanism of hydrolysis of esters. (*Andhra B.Sc. 1978*)

15. Give two characteristic reactions of ethyl nitrite and nitroethane.
(*Madras B.Sc. 1978*)

16. How is ethyl acetate prepared ? Give the mechanism for an ester formation. What are its properties ? Give the mechanism for the following reactions of an ester :

(*a*) Hydrolysis.

(*b*) When reacts with Grignard reagent. (*Sri Venkateswara B.Sc. 1978*)

17. How will you distinguish between : Ethyl nitrite and nitroethane.
(*Kanpur B.Sc. 1977*)

27

Amines

1. **Amines are Alkyl Ammonias.**—Derivatives of ammonia, in which one or more hydrogen atoms have been replaced by alkyl groups, are called **Amines**. These are further classified as ***Primary***, ***Secondary*** or ***Tertiary Amines*** according as one, two or three hydrogen atoms of ammonia are replaced by alkyl groups.

NH_3 — Ammonia

RNH_2 — Alkylamine (*Primary*)

R_2NH — Dialkylamine (*Secondary*)

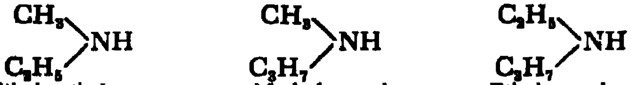
R_3N — Trialkylamine (*Tertiary*)

Thus the characteristic groups of the three types of amines are the *amino group*, $-NH_2$, the *imino group*, $>NH$ and the *tertiary nitrogen atom*, $\equiv N$ respectively.

In addition to the primary, secondary and tertiary amines tetra-alkyl derivatives of ammonium hydroxide, $[R_4N]^+OH^-$ are also known. These are termed tetra-alkylammonium hydroxides or quaternary ammonium hydroxides.

2. **Nomenclature.**—Individual members derive their names from the alkyl groups attached to the nitrogen atom. Each name ends with the suffix *amine*, *e.g.*,

$CH_3.NH_2$	$C_4H_9NH_2$	$(CH_3)_2NH$	$(CH_3)_3N$
Methylamine	Butylamine	Dimethylamine (*Simple*)	Trimethylamine (*Simple*)



$(CH_3)(C_2H_5)NH$ — Ethylmethylamine (*Mixed*)

$(CH_3)(C_3H_7)NH$ — Methylpropylamine (*Mixed*)

$(C_2H_5)(C_3H_7)NH$ — Ethylpropylamine (*Mixed*)

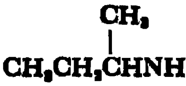
When all the alkyl groups attached to the nitrogen atom are the same, the amine is said to be *simple*. It is called a mixed amine when the alkyl groups are different.

The quaternary compounds are named as illustrated in the example below :

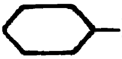
Tetramethylammonium hydroxide—$[(CH_3)_4N]OH$

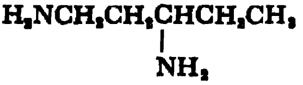
Tetraethylammonium iodide—$[(C_2H_5)_4N]^+I^-$

IUPAC names. Primary monoamines are preferably named substitutively by adding the suffix *amine* to the name of the chain or ring system to which the NH_2 group is attached, with the elision of the terminal *e* in names. For polyamines the suffixes diamine, triamine, etc. are used. For example



$CH_3CH_2\underset{}{\overset{CH_3}{\overset{|}{C}}}HNH_2$ is named as 2-Butanamine.

—NH_2 is Cyclohexanamine



$H_2NCH_2CH_2\underset{\underset{NH_2}{|}}{C}HCH_2CH_3$ is 1, 3- Pentanediamine

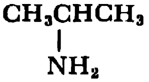
Secondary and tertiary amines are preferably named substitutively as derivatives of the highest ranking primary amine structure. For example,

$CH_3\,CH_2CH_2NHCH_3$ is *N*-Methyl-1-propanamine

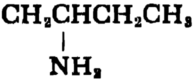
$CH_3.CH_2N(CH_3)_2$ is *N*, *N*-Dimethylethanamine.

As alternatives to alkanamine-type names for primary amines and symmetrical acyclic secondary and tertiary monoamines, substitutive names based on *amine*, are acceptable. For example

$CH_3CH_2NHCH_2CH_3$	*N*-Ethylethanamine or Diethylamine
$(CH_3CH_2)_3N$	*N*,*N*-Diethylethanamine or Triethylamine
CH_3NH_2	Methanamine or Methylamine



$CH_3\underset{\underset{NH_2}{|}}{C}HCH_3$ 2-Propanamine or Isopropylamine,



$CH_2\underset{\underset{NH_2}{|}}{C}HCH_2CH_3$ 2-Butanamine or *sec*-Butylamine

3. General Methods of Preparation.—Different methods for preparation of various amines are :

Methods yielding mixture of amines :

(*i*) **Hofmann's method.** *By heating alkyl halide with alcoholic ammonia in a sealed tube.* A mixture of primary, secondary and tertiary amines along with the quaternary compound are produced and have to be separated.

$$CH_3\boxed{I\ +\ H}\underset{\text{Ammonia}}{NH_2} \rightarrow \underset{\text{Methylamine}}{CH_3NH_2} + HI$$

$$\underset{\text{Methylamine}}{CH_3NH}\boxed{{}_2\ +\ I}CH_3 \rightarrow \underset{\text{Dimethylamine}}{(CH_3)_2NH} + HI$$

$$\underset{\text{Dimethylamine}}{(CH_3)_2N}\boxed{H\ +\ I}CH_3 \rightarrow \underset{\text{Trimethylamine}}{(CH_3)_3N} + HI$$

$$\underset{\text{Trimethyl-amine}}{(CH_3)_3N} + \underset{\text{Methyl iodide}}{CH_3I} \rightarrow \underset{\text{Tetramethyl-ammonium iodide}}{(CH_3)_4N{-}I}$$

The primary amine may be obtained in a good yield by using a large excess of ammonia. Tertiary amine may, however, be obtained in good yield by using alkyl halide in slight excess than required by the equation :

$$3RX + NH_3 \longrightarrow R_3N + 3HX$$

Ammonolysis of alkyl halides is a nucleophilic substitution (*for details refer to alkyl halides*).

$$H_3N: + R{-}X \rightarrow \underset{\text{Transition complex}}{\left[\overset{+\delta}{H_3N}\cdots\cdots R\cdots\cdots\overset{-\delta}{X}\right]} \longrightarrow H_3\overset{+}{N}{-}R + \overset{-}{X}$$

The salt obtained on decomposition with alkali liberates the amine. Primary alkyl halides give the best yield while in case of tertiary alkyl halides *elimination* reaction is the main reaction and an olefin is formed (compare the reaction with KOH).

(*ii*) **By ammonolysis of alcohols.** *By passing the mixture of the vapours of alcohol and ammonia over heated alumina* (*623K*). Here again mixture of three amines is obtained.

$$CH_3\boxed{OH \;+\; H}NH_2 \longrightarrow CH_3NH_2 \quad + \quad H_2O$$

$$\underset{\text{Methylamine}}{CH_3NH}\boxed{H \;+\; HO}CH_3 \longrightarrow \underset{\text{Dimethylamine}}{(CH_3)_2NH} \quad + \quad H_2O$$

$$\underset{\text{Dimethylamine}}{(CH_3)_2N}\boxed{H \;+\; HO}CH_3 \longrightarrow \underset{\text{Trimethylamine}}{(CH_3)_3N} \quad + \quad H_2O$$

The primary amine may be obtained as the main product by using a large excess of ammonia.

The separation of the mixture of amines obtained by any of the methods is effected as described on page 2·304.

Methods yielding Primary amines :

(*i*) **Hofmann's Bromamide Reaction.** *By the action of bromine and caustic potash on amides* (*see* page 2·269).

$$\underset{\text{Acetamide}}{CH_3CONH_2} + Br_2 + 4KOH \rightarrow \underset{\text{Methylamine}}{CH_3NH_2} + 2KBr + K_2CO_3 + 3H_2O$$

This is generally the most convenient method for preparing primary amines.

(*ii*) *By the reduction of nitroparaffins with metal and acid or with hydrogen in the presence of nickel or with* $LiAlH_4$.

$$\underset{\text{Nitroethane}}{C_2H_5NO_2} + 3H_2 \xrightarrow{Ni} \underset{\text{Ethylamine}}{C_2H_5NH_2} + 2H_2O \qquad \text{(ss.)}$$

(*iii*) *By the reduction of oximes with sodium and ethanol or catalytically.*

$$\underset{\text{Acetaldoxime}}{CH_3CH{=}NOH} + 4[H] \rightarrow \underset{\text{Ethylamine}}{CH_3CH_2NH_2} + H_2O \qquad (g.)$$

(*iv*) **Mendius' Reaction.** *By the reduction of alkyl cyanide catalytically or with sodium in alcohol or with* $LiAlH_4$.

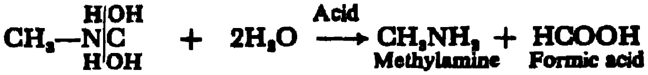
$$\underset{\text{Methyl cyanide}}{CH_3C{\equiv}N} + 4[H] \rightarrow \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$$

High molecular weight amines are easily obtained by this method since the cyanides can be readily prepared from long chain fatty acids.

(*v*) *By the reduction of amides with* $LiAlH_4$.

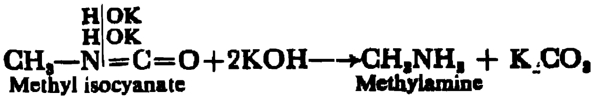
$$RCONH_2 + 4H \longrightarrow RCH_2NH_2 + H_2O$$

(*vi*) *By the hydrolysis of alkyl isocyanides with dilute acid and hydrolysis of alkyl isocyanates with boiling alkalis.*



$$CH_3—N\overset{H\ OH}{\underset{H\ OH}{C}} + 2H_2O \xrightarrow{\text{Acid}} CH_3NH_2 + HCOOH$$

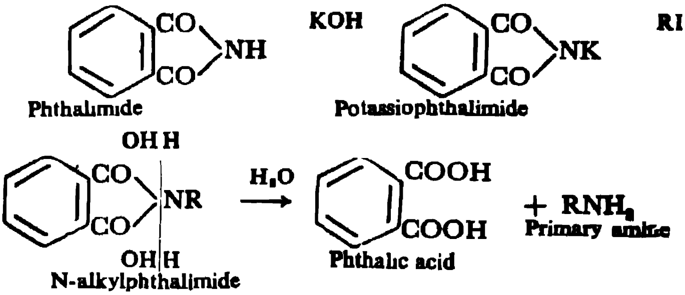
Methylamine Formic acid



$$CH_3—N\overset{H\ OK}{\overset{H\ OK}{=}}C=O + 2KOH \longrightarrow CH_3NH_2 + K_2CO_3$$

Methyl isocyanate Methylamine

(*vii*) **Gabriel's Phthalimide synthesis.** Phthalimide is treated with alcoholic potash to get potassiophthalimide which gives N-alkyl phthalimide when heated with an alkyl halide. This is heated with 20 per cent hydrochloric acid under pressure or refluxed with caustic potash solution when phthalic acid and a primary amine are obtained as a result of hydrolysis.

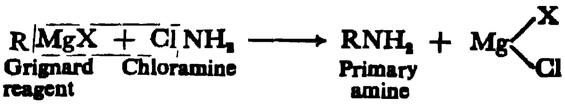


(*viii*) *By decarboxylation of Amino acids*—by distilling them with barium hydroxide or by putrefying bacteria.

$$CH_2.NH_2.COOH \xrightarrow{Ba(OH)_2} CH_3NH_2 + CO_2$$

Aminoacetic acid Methylamine

(*ix*) *By means of a Grignard reagent and chloramine.*



$$R|MgX + Cl|NH_2 \longrightarrow RNH_2 + Mg\langle{}^{X}_{Cl}$$

Grignard reagent Chloramine Primary amine

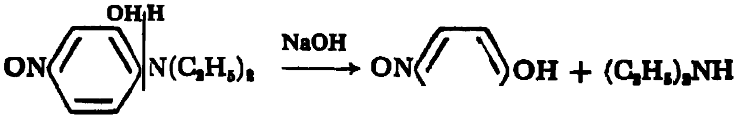
Methods yielding Secondary amines :

(*i*) *By heating the primary amine with calculated quantity of alkyl halide.*

$$RNH_2 + IR \longrightarrow R_2NH + HI$$

Primary amine Secondary amine

(*ii*) *By heating p-nitroso-dialkylaniline with strong alkali solution a pure secondary amine is obtained.*



p-nitroso-diethylaniline *p*-nitroso-phenol diethylamine

This is one of the best methods for preparing pure secondary amines.

(*iii*) *By reduction of an alkyl isocyanide with nascent hydrogen or catalytically.*

$$\underset{\text{Alkyl isocyanide}}{R.NC} + 4[H] \longrightarrow \underset{\text{Secondary amine}}{R.NH.CH_3}$$

(*iv*) *By the hydrolysis of a dialkyl cyanamide with an acid or alkali.*

$$\underset{\substack{\text{Calcium}\\ \text{cyanamide}}}{CaN.CN} \xrightarrow{NaOH} \underset{\substack{\text{Sodium}\\ \text{cyanamide}}}{Na_2N.CN} \xrightarrow{RX} \underset{\substack{\text{Dialkyl}\\ \text{cyanamide}}}{R_2N.CN}$$

$$R_2N.CN \xrightarrow{H_2O} \underset{\text{sec. amine}}{R_2NH} + CO_2 + NH_3$$

Methods yielding Tertiary amines :

(*i*) *By heating an alcoholic solution of ammonia with slight excess of alkyl halide than required by the equation* :

$$3RX + \underset{(Alcoholic)}{NH_3} \rightarrow \underset{\text{Tertiary amine}}{R_3N} + 3HX$$

(*ii*) *By the thermal decomposition of quaternary ammonium hydroxide.* A quaternary ammonium halide is treated with moist silver oxide and the quaternary ammonium hydroxide obtained is heated. Tetramethylammonium hydroxide decomposes to give an alcohol whereas all others give an olefin and water.

$$[(CH_3)_4N]X + AgOH \rightarrow [(CH_3)_4N]OH + AgX$$

$$\underset{\substack{\text{Tetramethylammonium}\\ \text{hydroxide}}}{[(CH_3)_4N]OH} \rightarrow \underset{\text{Trimethylamine}}{(CH_3)_3N} + CH_3OH$$

$$\underset{\substack{\text{Tetraethylammonium}\\ \text{hydroxide}}}{[(C_2H_5)_4N]OH} \rightarrow \underset{\text{Triethylamine}}{(C_2H_5)_3N} + C_2H_4 + H_2O$$

Nature of olefin obtained is governed by Hofmann rule (*see* page 2·21).

4. **Separation of Amine Mixtures.**—The mixture of the amine salts and the quaternary salt is distilled with potassium hydroxide solution when the three amines distil over, leaving the quaternary salt behind in solution.

$$RNH_2.HI + KOH \rightarrow RNH_2 + KI + H_2O$$

The mixture of the three amines in the distillate is separated into the individual amines by one of the following methods :

(*i*) **Fractional Distillation.** The mixture is subjected to fractional distillation and separated into its constituents. It has proved to be the most satisfactory industrial method as highly efficient fractionating columns are available.

(*ii*) **Hinsberg's Method.** The mixture is treated with benzenesulphonyl chloride—$C_6H_5SO_2Cl$ (*Hinsberg's reagent*) and then some alkali and ether are added. Primary amine forms a sulphonamide which dissolves in alkali forming its sodium salt. This comes in the lower aqueous layer.

$$C_2H_5NH_2 + C_6H_5SO_2Cl \longrightarrow C_2H_5NH.SO_2C_6H_5 + HCl$$

Ethylamine (*Primary*)

Hinsberg's reagent (*Benzene-sulphony chloride*)

Sulphonamide

$$C_2H_5NH.SO_2C_6H_5 \xrightarrow{\text{alkali}} C_2H_5NNa.SO_2C_6H_5$$

(*Soluble in water*)

Secondary amines form a sulphonamide which comes in the upper ethereal layer along with the tertiary amine which is not reacted.

$$(C_2H_5)_2NH + C_6H_5SO_2Cl \longrightarrow (C_2H_5)_2N.SO_2C_6H_5 + HCl$$

Diethylamine (*Secondary*) Sulphonamide (*Insol. in alkali*)

The two layers are separated and tertiary amine obtained from the ether layer by fractional distillation. The other fraction (sulphonamide of secondary amine) is treated with concentrated hydrochloric acid when secondary amine is generated by hydrolysis and passes over when the mixture is distilled over caustic soda.

$$(C_2H_5)_2N.SO_2C_6H_5 + HCl + H_2O \longrightarrow C_6H_5SO_2OH + (C_2H_5)_2NH.HCl$$

Sulphonamide of sec. amine

$$(C_2H_5)_2NH.HCl + NaOH \longrightarrow (C_2H_5)_2NH + NaCl + H_2O$$

sec. amine hydrochloride secondary amine

The aqueous layer is acidified with dilute hydrochloric acid and then hydrolysed with concentrated hydrochloric acid. This is then distilled over sodium hydroxide when primary amine passes over.

$$C_2H_5NNaSO_2C_6H_5 + HCl \longrightarrow C_2H_5NHSO_2C_6H_5 + NaCl$$

Sod. salt of sulphonamide of primary amine Sulphonamide of primary amine

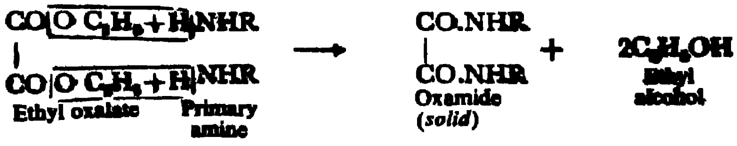
$$C_2H_5NH.SO_2C_6H_5 + HCl + H_2O \longrightarrow C_2H_5NH_2.HCl + C_6H_5SO_2.OH$$

Primary amine hydrochloride

$$C_2H_5NH_2.HCl + NaOH \longrightarrow C_2H_5NH_2 + NaCl + H_2O$$

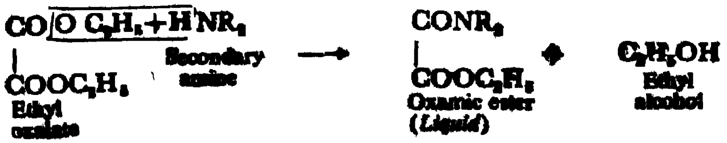
Primary amine hydrochloride Primary amine

(*iii*) **Hofmann's Method.** Here the mixture is treated with diethyl oxalate which gives a solid oxamide with primary amine, a liquid oxamic ester with secondary amine while the tertiary amine does not react.



$$\begin{matrix} CO\boxed{OC_2H_5 + H}NHR \\ | \\ CO\boxed{OC_2H_5 + H}NHR \end{matrix} \longrightarrow \begin{matrix} CO.NHR \\ | \\ CO.NHR \end{matrix} + 2C_2H_5OH$$

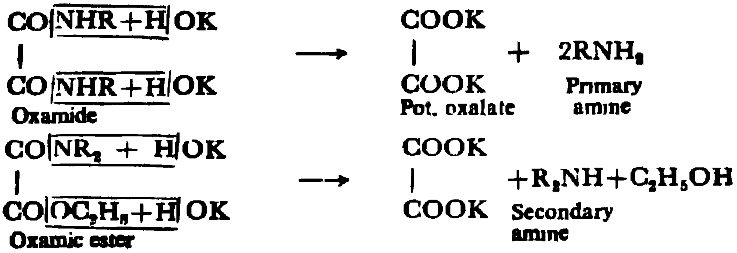
Ethyl oxalate Primary amine Oxamide (*solid*) Ethyl alcohol



$$\begin{matrix} CO\boxed{OC_2H_5 + H}NR_2 \\ | \\ COOC_2H_5 \end{matrix} \longrightarrow \begin{matrix} CONR_2 \\ | \\ COOC_2H_5 \end{matrix} + C_2H_5OH$$

Ethyl oxalate Secondary amine Oxamic ester (*Liquid*) Ethyl alcohol

The solid oxamide is separated and heated with caustic potash when primary amine is obtained. The liquid (mixture of oxamic ester+tertiary amine) is subjected to fractional distillation. Oxamic ester is again decomposed by heating with caustic potash to get secondary amine.



$$\begin{array}{l} CO\boxed{NHR+H}OK \\ | \\ CO\boxed{NHR+H}OK \\ \text{Oxamide}\end{array} \longrightarrow \begin{array}{l} COOK \\ | \\ COOK \\ \text{Pot. oxalate}\end{array} + \underset{\text{Primary amine}}{2RNH_2}$$

$$\begin{array}{l} CO\boxed{NR_2 + H}OK \\ | \\ CO\boxed{OC_2H_5+H}OK \\ \text{Oxamic ester}\end{array} \longrightarrow \begin{array}{l} COOK \\ | \\ COOK \end{array} + \underset{\text{Secondary amine}}{R_2NH} + C_2H_5OH$$

5. General Properties : Physical. (*i*) The lower members are gases followed by others which are liquids. Higher ones are solids.

(*ii*) Lower members are soluble in water due to hydrogen bonding but the solubility decreases as the molecular weight increases and hydrocarbon group becomes bulky.

(*iii*) The lower members have a powerful fishy smell and are combustible. The odour fades with increase of molecular weight.

(*iv*) Their boiling points show a regular gradation—rise gradually with increase of molecular weight.

Physical Properties of some Typical Amines

Formula	*Name*	*B.P.* (*K*)	*Solubility in water*
CH_3NH_2	Methylamine	266	Very soluble
$C_2H_5NH_2$	Ethylamine	292	Very soluble
$(CH_3)_3N$	Trimethylamine	277	Very soluble
$(C_2H_5)_3N$	Triethylamine	363	Slightly soluble
$C_6H_{11}NH_2$	Cyclohexylamine	407	Slightly soluble
$C_6H_5NH_2$	Aniline (Phenylamine)	457	Insoluble

Chemical. The chemistry of primary and secondary amines is comparable with that of alcohols, that of tertiary amines with that of ethers and that of alkyl ammonium ions with that alkyloxonium ions.

$$CH_3NH_2,\ (CH_3)_2NH \qquad (CH_3)_3N \qquad (CH_3)_4\overset{\oplus}{N} \qquad (CH_3)_3\overset{\oplus}{N}H$$

$$CH_3OH \qquad (CH_3)_2O \qquad (CH_3)_3\overset{\oplus}{O} \qquad (CH_3)_2\overset{\oplus}{O}H$$

Their reactions can be discussed under the following heads :

(A) Reactions of the lone-pair electrons of Amines. All amines have a lone pair of electrons and reactions involving this lone pair as given below are an important aspect of the chemistry of amines.

(1) **Basic Nature.** Since the lone pair can be used to form a bond to a proton, the amines are basic in nature. Lower members are stronger bases than ammonia. These are stronger bases than water and alcohols but weaker than hydroxide ion.

(*a*) ***With water amines give alkylammonium hydroxides*** which ionize to give hydroxide ions in solution (*cf.* ammonia which gives ammonium hydroxide).

$$RNH_2 + H_2O \rightleftharpoons RNH_3.OH \rightleftharpoons [RNH_3]^+ + OH^-$$
$$R_2NH + H_2O \rightleftharpoons R_2NH_2.OH \rightleftharpoons [R_2NH_2]^+ + OH^-$$
$$R_3N + H_2O \rightleftharpoons R_3NH.OH \rightleftharpoons [R_3NH]^+ + OH^-$$

Thus aqueous solutions of amines are alkaline in nature. These absorb carbon dioxide, give ferric hydroxide precipitate with ferric chloride and blue solution with copper sulphate.

Mono-, di-, and trialkyl ammonium ions are weakly acidic in aqueous solutions. These react with a strong base and lose a proton to liberate the amine.

$$(CH_3)_2\overset{\oplus}{N}H_2 + \overset{\ominus}{O}H \longrightarrow (CH_3)_2NH + H_2O$$

Tetralkylammonium ions are not acidic since these have no proton on the positively charged nitrogen.

Basicity of amines will be controlled by the availability of the lone pair for protonation. At first sight, it would appear that as the number of alkyl groups increases, the lone pair will become more available due to the +I effects of the alkyl groups and the basicity of the amine will increase on alkylation. This, however, is not the case and the order of the basicity is :

Alkyl Groups	*Relative Base Strength*
CH_3—	$R_2NH > RNH_2 > R_3N > NH_3$
C_2H_5—	$R_2NH > RNH_2 > NH_3 > R_3N$
$(CH_3)_2CH$—	$RNH_2 > NH_3 > R_2NH > R_3N$
$(CH_3)_3C$—	$NH_3 > RNH_2 > R_2NH > R_3N$

Two reasons suggested for this order are :

(*i*) *Steric effect.* Addition of proton increases crowding resulting in strain which is maximum in tertiary amines. As a result the stability of this molecule is reduced, *i.e.*, its basicity is reduced.

This is borne out by the fact that as the size of the alkyl group increases thereby increasing the steric repulsion in the salts, the relative base strengths diminish until finally ammonia is the strongest base.

(*ii*) *Decrease in Solvation.* All 'onium ions carry a positive charge and are stabilised due to solvation. The greater the size of the ion, the less will be the solvation and the less stabilised is the ion.

In passing from secondary amine to tertiary amine the availability of the lone pair increases but the size of ion increases so much that it is less solvated. *Stabilisation lost due to this decrease in solvation is greater than the inductive effect making the lone pair available for protonation.*

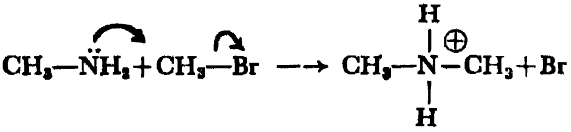
(*b*) *With acids they give salts*, *e.g.*, ethylamine combines with hydrochloric acid to give ethylammonium chloride.

$$\underset{\text{Ethylamine}}{C_2H_5NH_2} + HCl \longrightarrow \underset{\text{Ethylammonium chloride}}{[C_2H_5NH_3]^+Cl^-}$$

To show their relationship to the amines, the salts are often written as $C_2H_5.NH_2.HCl$ ethylamine hydrochloride, $(CH_3NH_2)_2.H_2SO_4$, methylamine sulphate.

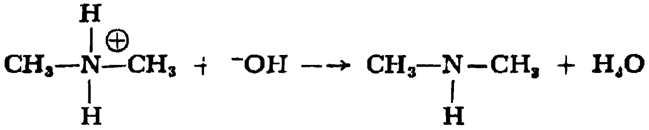
Amine salts of chloroplatinic acid, H_2PtCl_6 are used for the determination of molecular weight of amines.

(2) **Alkylation.** Amines are nucleophilic due to lone pair of electrons and can form a bond to carbon. They react faster than alcohols or water. For example, they react with alkyl halides to form a new N—C bond.



$$CH_3-\ddot{N}H_2+CH_3-Br \longrightarrow CH_3-\overset{H}{\underset{H}{\overset{|\oplus}{N}}}-CH_3+Br$$

The ammonium ion produced loses a proton to a base to form dimethylamine.



$$CH_3-\overset{H}{\underset{H}{\overset{|\oplus}{N}}}-CH_3 + {}^{-}OH \longrightarrow CH_3-\underset{H}{N}-CH_3 + H_2O$$

Thus on treating an amine with alkyl halide, hydrogen atoms of the ammonia residue are successively replaced by alkyl groups. Finally, the tertiary amine adds one more molecule of alkyl halide to form a quaternary compound.

$$CH_3NH_2 \xrightarrow[-HI]{CH_3I} (CH_3)_2NH \xrightarrow[-HI]{CH_3I} (CH_3)_3N \xrightarrow{CH_3I} (CH_3)_4NI$$

Methylamine (*Primary*)	Dimethylamine (*Secondary*)	Trimethylamine (*Tertiary*)	Tetramethylammonium iodide

When an amine salt is heated at high temperature, a molecule of alkyl halide is eliminated (*Reverse of alkylation*).

$$\underset{\textit{tert.}\text{ amine salt}}{R_3N.HCl} \xrightarrow{\text{Heat}} \underset{\textit{sec.}\text{ amine}}{R_2NH} + RCl$$

$$\underset{\textit{sec.}\text{ amine salt}}{R_2NH.HCl} \longrightarrow \underset{\textit{p.}\text{ amine}}{RNH_2} + RCl$$

$$\underset{\textit{p.}\text{ amine salt}}{RNH_2.HCl+HCl} \longrightarrow NH_4Cl + RCl$$

(3) **Acylation.** Acid chlorides react with primary and secondary amines and replace hydrogen atoms of the amino group by acyl group. (*Formation of new N—C bond as in alkylation*).

$$\underset{\substack{\text{Methylamine}\\(\textit{Primary})}}{CH_3NH}\boxed{{}_2\ +\ Cl}\underset{\substack{\text{Acetyl}\\\text{chloride}}}{COCH_3} \longrightarrow \underset{\substack{\text{Acetylmethylamine}\\\text{or } N\text{-Methylacetamide}}}{CH_3NH.COCH_3} + HCl$$

$$\underset{\substack{\text{Dimethylamine}\\(\textit{Secondary})}}{(CH_3)_2N}\boxed{H\ +\ Cl}COCH_3 \longrightarrow \underset{\substack{\text{Acetyldimethylamine}\\\text{or } N,N\text{-Dimethylacetamide}}}{(CH_3)_2N.COCH_3} + HCl$$

Tertiary amines are not acylated.

(B) Reactions of the N—H Bonds.

(4) **Deprotonation.** Amines can be deprotonated only by very strong bases.

$$(C_2H_5)_2NH + CH_3Li \longrightarrow (C_2H_5)_2\overset{\ominus}{N}\ \overset{\oplus}{Li} + CH_4$$

However, as stated before, alkylammonium ions with at least one N—H bond readily donate a proton to water.

(5) **Action of Sodium.** Primary and secondary amines form sodium salts when heated with sodium.

$$2RNH_2 + 2Na \longrightarrow 2[RNH]^-Na^+ + H_2$$
$$2R_2NH + 2Na \longrightarrow 2[R_2N]^-Na^+ + H_2$$

(6) **Action of Halogens.** Primary and secondary amines react with halogens in the presence of alkali to form **halogeno amines.**

$$\underset{\text{Primary amine}}{R.NH_2} \xrightarrow{X_2/NaOH} \underset{\text{Monohalogeno derivative}}{R.NHX} \xrightarrow{X_2/NaOH} \underset{\text{Dihalogeno derivative}}{R.NX_2}$$

$$\underset{\text{Secondary amine}}{R_2NH} \xrightarrow{X_2/NaOH} \underset{\text{Monohalogeno derivative}}{R_2NX}$$

(7) **Action of Nitrous acid.**

(*i*) *Primary amines* form alcohols with the liberation of nitrogen.

$$\underset{\text{Primary amine}}{\begin{array}{c|c|l} HO & N & O \\ R & N & H_2 \end{array}} + HONO \longrightarrow \underset{\text{Alcohol}}{ROH} + N_2 + H_2O$$

(*ii*) *Secondary amines* form nitrosoamines (yellow oily liquids).

$$\underset{\text{Secondary amine}}{R_2N|\overline{H \;+\; HO}|NO} \longrightarrow \underset{\text{Nitrosoamine}}{R_2N.NO} + H_2O$$

Nitrosoamines on warming with phenol and concentrated sulphuric acid give a brown or red colour which soon changes blue-green. The colour changes red on dilution and further changes blue or violet on treating with alkali. This is **Liebermann's nitroso reaction** used for treating secondary amines.

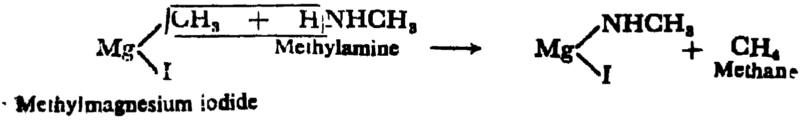
(*iii*) *Tertiary amines* dissolve in cold nitrous acid to form salt, $R_3N.HNO_2$. This on warming decomposes to give a nitrosoamine and alcohol.

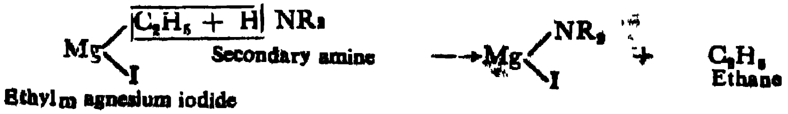
$$R_3N.HNO_2 \longrightarrow R_2N.NO + ROH$$

(8) **Carbylamine reaction.** When heated with chloroform and alcoholic potash, primary amines give an offensive smell of carbylamine. Secondary and tertiary amines do not give this test.

$$\underset{\substack{\text{Ethylamine}\\(\textit{Primary})}}{C_2H_5N}|\overline{H_2 \;+\; \underset{\text{Chloroform}}{Cl_3H}}|C + \underset{\substack{\text{Alcoholic}\\\text{potash}}}{3KOH} \longrightarrow \underset{\substack{\text{Ethyl}\\\text{isocyanide}}}{C_2H_5NC} + 3KCl + 3H_2O$$

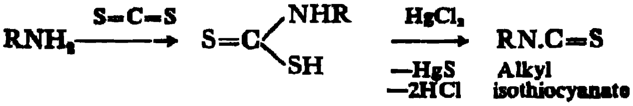
(9) **Action with Grignard reagents.** Primary and secondary amines give hydrocarbons with Grignard reagents. Tertiary amines do not react.





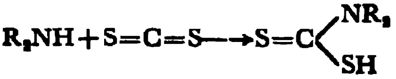
(10) **Warming with Carbon disulphide.**

(a) **Primary amines** form an alkyl derivative of dithiocarbamic acid which is decomposed by mercuric chloride to give alkyl iso-thiocyanate. This is *Hofmann's mustard oil reaction* used as a test for primary amines.



$$RNH_2 \xrightarrow{S=C=S} S=C\begin{cases}NHR\\SH\end{cases} \xrightarrow[-HgS,\ -2HCl]{HgCl_2} \underset{\text{Alkyl isothiocyanate}}{RN.C=S}$$

(b) Secondary amines form a dialkyl derivative of dithiocarbamic acid which is not decomposed by mercuric chloride.



$$R_2NH+S=C=S \longrightarrow S=C\begin{cases}NR_2\\SH\end{cases}$$

(11) **Oxidation.** All the three types of amines can be oxidised. The product depends on the nature of oxidising agent, class of amine and nature of alkyl group.

(a) *Primary amines.*

$$RCH_2.NH_2 \xrightarrow[{[O]}]{KMnO_4} \underset{\text{Aldimine}}{RCH=NH} \xrightarrow{H_2O} RCHO + NH_3$$

$$R_2CH.NH_2 \xrightarrow[{[O]}]{KMnO_4} \underset{\text{Ketimine}}{R_2C=NH} \xrightarrow{H_2O} R_2CO + NH_3$$

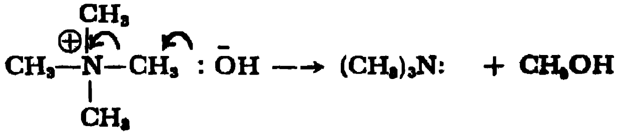
(b) *Secondary amines.*

$$\underset{\text{Dialkyl-hydroxylamine}}{R_2N.OH} \xleftarrow[\text{Caro's acid}]{H_2SO_5} R_2NH \xrightarrow{KMnO_4} \underset{\text{Tetra-alkylhydrazine}}{R_2N-NR_2}$$

(c) *Tertiary amines* are not affected by potassium permanganate but are oxidised by Caro's acid or Fenton's reagent to amine oxides.

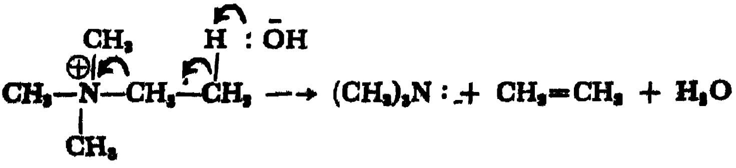
$$\underset{\textit{tert.}\text{ amine}}{R_3N} + [O] \longrightarrow \underset{\text{Amine oxide}}{R_3N{\to}O}$$

(C) **Reactions involving N—C Bonds.** Cleavage of N—C bonds of alkylammonium ions can occur if the ion can undergo attack by a nucleophile at the carbon atom.



$$(CH_3)_4\overset{\oplus}{N} + :\overset{-}{O}H \longrightarrow (CH_3)_3N: + CH_3OH$$

Cleavage of N—C bond also occurs by nucleophilic attack at a β-hydrogen atom with the elimination of an amine.



$$(CH_3)_3\overset{\oplus}{N}-CH_2-CH_2H + :\overset{-}{O}H \longrightarrow (CH_3)_3N: + CH_2=CH_2 + H_2O$$

INDIVIDUAL MEMBERS

7. **Methylamine, CH_3NH_2.**—Methylamine can be prepared by the general methods of preparation of primary amines. It is, however, conveniently prepared in the laboratory by Hofmann's Bromamide Reaction (*see* page 2·30).

Expt. Mix equivalent amounts of bromine and acetamide in a distillation flask and add slowly 10% caustic potash solution until the reddish colour of bromine is just discharged. The mixture now contains a solution of acetobromide. To this is added an excess of concentrated solution (50%) of caustic potash and the flask warmed gently on a water bath at 330-340K. When the solution becomes nearly colourless, it is distilled and methylamine which distils over is absorbed in dilute hydrochloric acid.

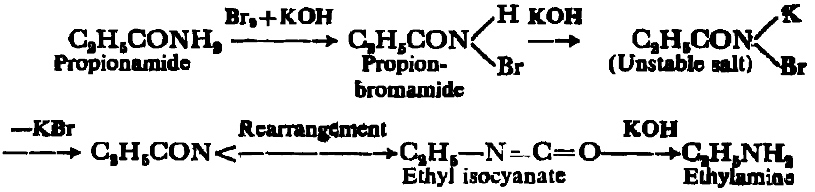
It can also be prepared by heating ammonium chloride with two equivalents of formaldehyde (in formalin solution). The yield is 45-51% based on the ammonium chloride.

$$2HCHO + NH_4Cl \longrightarrow CH_3NH_2.HCl + HCOOH$$

It is prepared industrially by passing a mixture of methyl alcohol and ammonia over a catalyst and separating methylamine from the mixture of amines obtained by fractional distillation.

Methylamine is a colourless gas (b.p. 266K) highly soluble in water, having a strong ammoniacal smell. Chemically it is a typical primary amine and is used as refrigerant.

8. **Ethylamine, $C_2H_5NH_2$.**—It can be prepared by any of the general methods for the preparation of primary amines but it is *prepared in the laboratory* by Hofmann's Bromamide Reaction as described under methylamine with the only difference that acetamide is replaced by propionamide.



$$\underset{\text{Propionamide}}{C_2H_5CONH_2} \xrightarrow{Br_2+KOH} \underset{\text{Propion-bromamide}}{C_2H_5CON\begin{smallmatrix}H\\Br\end{smallmatrix}} \xrightarrow{KOH} \underset{\text{(Unstable salt)}}{C_2H_5CON\begin{smallmatrix}K\\Br\end{smallmatrix}}$$

$$\xrightarrow{-KBr} C_2H_5CON< \xrightarrow{\text{Rearrangement}} \underset{\text{Ethyl isocyanate}}{C_2H_5{-}N{=}C{=}O} \xrightarrow{KOH} \underset{\text{Ethylamine}}{C_2H_5NH_2}$$

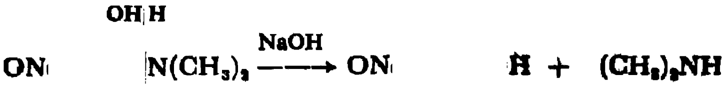
It can be prepared on a commerical scale by heating ethylene and ammonia under pressure at about 670K in the presence of cobalt catalyst when ethylamine and diethylamine both are produced.

$$\underset{\text{Ethylene}}{CH_2{=}CH_2} + \underset{\text{Ammonia}}{HNH_2} \xrightarrow[670K]{\text{Co-cat}} \underset{\text{Ethylamine}}{CH_3{-}CH_2{-}NH_2}$$

$$2CH_2{=}CH_2 + NH_3 \longrightarrow \underset{\text{Diethylamine}}{(C_2H_5)_2NH}$$

Ethylamine is a colourless, inflammable liquid (b.p. 292K) with a fishy ammoniacal odour. It is highly soluble in water and gives all the general reactions of a primary amine.

9. **Dimethylamine, $(CH_3)_2NH$.**—A pure sample of dimethylamine is prepared by heating *p*-nitroso-dimethylaniline with strong alkali solution.



p-nitroso-dimethylaniline *p*-nitrosophenol Dimethylamine

It can also be prepared by heating ammonium chloride with four equivalents of formaldehyde.

$$4HCHO+NH_4Cl \longrightarrow \underset{\text{Dimethylamine hydrochloride}}{(CH_3)_2NH.HCl} + 2HCOOH$$

It is a colourless gas (b.p. 280K) with an ammoniacal smell and finds use in dehairing hides and as a rubber accelerator. Chemically it is a typical secondary amine.

10. Trimethylamine, $(CH_3)_3N$.—It occurs in the excreta of fish and is present in some plants and in the distillate from beet sugar molasses. In the laboratory, it is conveniently prepared by heating tetramethylammonium hydroxide (*see* next page).

Trimethylamine is manufactured by heating a solid mixture of ammonium chloride and paraformaldehyde.

$$2NH_4Cl + 9HCHO \rightarrow 2(CH_3)_3N.HCl+3CO_2+3H_2O \quad (89\%)$$

It is a colourless gas (b.p. 276·5K) and is used as a source of methyl chloride.

$$(CH_3)_3N + 4HCl \xrightarrow{\text{Heat ; pressure}} 3CH_3Cl + NH_4Cl$$

11. Distinguishing Tests between Primary, Secondary and Tertiary Amines.—The various tests which may be employed to distinguish between three types of amines are tabulated below :

Test	Primary amines	Secondary amines	Tertiary amines
1. Treat with nitrous acid.	Form alcohols with the evolution of nitrogen (*see* page 2·309).	Form only nitroso amines which give Lieberman's nitroso reaction (*see* page 2·309).	Form only the nitrites in cold.
2. Treat with chloroform and alcoholic potash.	Give obnoxious smell of carbylamine (*see* page 2·309).	No action.	No action.
3. Treat with Hinsberg's reagent—benzenesulphonyl chloride.	Give sulphonamides soluble in caustic soda (*see* page 2·305).	Give sulphonamide insoluble in caustic soda (*see* page 2·305).	No action.
4. Treat with methyl iodide under ordinary pressure	No action	No action.	Give quaternary compounds.
5. Treat with acetyl chloride.	Give amides (*see* page 2·308).	Give amides (*see* page 2·308).	No action.

QUATERNARY AMMONIUM COMPOUNDS

12. Tetra-alkylammonium Halides.—These are prepared by the action of ammonia with excess of an alkyl halide or by the direct action between a tertiary amine and an alkyl halide.

$$\underset{\text{Trimethylamine (Tertiary)}}{(CH_3)_3N} + CH_3I \longrightarrow \underset{\text{Tetramethylammonium iodide (Quaternary cpd.)}}{(CH_3)_4NI}$$

Quaternary compounds are white crystalline compounds soluble in water. These are completely ionised in their aqueous solution.

$$(CH_3)_4NI \longrightarrow [(CH_3)_4N]^+ + I^-$$

These are decomposed on heating and yield tertiary amine

$$(CH_3)_4NI \xrightarrow{\text{Heat}} (CH_3)_3N + CH_3I$$

13. Tetra-alkylammonium Hydroxides.—These are prepared by the action of moist silver oxide on tetra-alkylammonium halides.

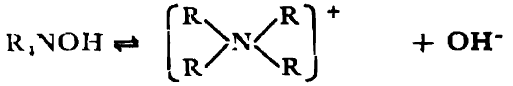
$$\underset{\text{Tetramethyl ammonium iodide}}{(CH_3)_4NI} + AgOH \longrightarrow \underset{\text{Tetramethylammonium hydroxide}}{(CH_3)_4NOH} + AgI$$

These are white, deliquescent crystalline solids, very soluble in water. On heating they decompose to give tertiary amines. Tetramethylammonium hydroxide gives trimethylamine and methanol. Higher members give *tert.* amine and an olefin.

$$\underset{\text{Tetramethylammonium hydroxide}}{(CH_3)_4NOH} \longrightarrow \underset{\text{Trimethylamine}}{(CH_3)_3N} + CH_3OH$$

$$\underset{\text{Tetraethylammonium hydroxide}}{(C_2H_5)_4NOH} \longrightarrow \underset{\text{Triethylamine}}{(C_2H_5)_3N} + C_2H_4 + H_2O$$

Quaternary compounds are strong bases (as strong as NaOH or KOH). This is because they are completely ionised in solution.



$$R_4NOH \rightleftharpoons [R_4N]^+ + OH^-$$

14. Ascent and Descent of Series.—Preparation of amines by reduction of alkyl cyanides of Hofmann's bromamide reaction are used for the Ascent and Descent of homologous series explained in the examples given below :

(*i*) *Conversion of Methylamine into Ethylamine* (**Ascent of series**).

$$\underset{\text{Methylamine}}{CH_3NH_2} \xrightarrow{HONO} \underset{\text{Methanol}}{CH_3OH} \xrightarrow{P+I_2} \underset{\text{Methyl iodide}}{CH_3I}$$

$$\xrightarrow{KCN} \underset{\text{Methyl cyanide}}{CH_3CN} \xrightarrow[Na/C_2H_5OH]{4[H]} \underset{\text{Ethylamine}}{CH_3.CH_2NH_2}$$

(*ii*) *Conversion of Ethylamine into Methylamine* (**Descent of series**).

$$\underset{\text{Ethylamine}}{C_2H_5NH_2} \xrightarrow{HONO} \underset{\text{Ethanol}}{C_2H_5OH} \xrightarrow{[O]} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{[O]} \underset{\text{Acetic acid}}{CH_3COOH}$$

$$\xrightarrow{NH_3} CH_3COONH_4 \xrightarrow{Heat} \underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow{Br_2+KOH} \underset{\text{Methylamine}}{CH_3NH_2}$$

QUESTIONS

Essay Type :

1. What are amines ? How are they classified ? Discuss the general methods of preparation and the properties of aliphatic amines.

2. Outline the methods available for the preparation of aliphatic primary amines. How may primary, secondary and tertiary aliphatic amines be distinguished and separated from one another ? (*Delhi B.Sc. 1977, 76*)

3. What are amines ? How may primary, secondary and tertiary aliphatic amines be separated from one another. (*Delhi B Sc. 1978 ; Madras 1978*)

4. (*a*) How many isomers of molecular formula C_2H_7N and C_3H_9N are possible ? Name them. (*Agra B.Sc. 1962*)

(*b*) The formula C_3H_9N represents several amines. Write the structural formulae of these isomers and illustrate by equations how each one of them reacts with (*i*) HNO_2, (*ii*) CH_3COCl, (*iii*) CS_2, and (*iv*) methyl iodide. (*Allahabad B.Sc 1966*)

5. How will you prepare the following :

(*a*) Ethyl isocyanide from ethylamine.

(*b*) *iso*-propyl chloride from *iso*-propylamine.

(*c*) Ethanol from Propionamide.

(*d*) Methylamine from Ethylamine and *vice versa*.

(*e*) Acetic acid from Propionic acid and *vice versa*.

(*f*) A primary amine into secondary amine and *vice versa*.

Short Answer Type :

1. How do primary, secondary and tertiary amines differ in their reaction towards nitrous acid ? (*Punjabi B.Sc. 1976*)

2. Give two chemical properties of Ethylamine. (*Punjabi B.Sc. 1976*)

3. Using Hinsberg's reagent, give a scheme to separate a mixture of *n*-propylamine, diethylamine and triethylamine into its constituents. (*Delhi B.Sc. 1976*)

4. How will you separate the constituents of a mixture of methylamine and dimethylamine ? Give one reaction to distinguish them. (*Delhi B.Sc. Hons. 1976*)

5. How are primary, secondary and tertiary amines distinguished from one another ? (Only two tests are required). (*Delhi B.Sc. 1976 Supp.*)

6. The amino group in ethylamine is basic whereas that in acetamide is not. Explain, why. (*Delhi B.Sc. Hons. 1976*)

7. Write a note on comparative strength of the primary, secondary and tertiary amines. (*Delhi B.Sc. 1977*)

8. How can you distinguish between methylamine, dimethylamine and trimethylamine ? (*Delhi B.Sc. Hons. Sub. 1978 Supp.*)

9. In which order does the basic strength vary in the series primary, secondary and tertiary aliphatic amines ? How do you explain this ? (*Madras B.Sc. 1977*)

10. What is carbylamine reaction ? (*Madras B.Sc. 1977*)

11. Why are tetraalkyl ammonium ions not acidic ?

12. How can you prepare propene from N : N-dimethylpropylamine ?

Problems :

1. With nitrous acid $C_2H_5O_2N$ (A) gives $C_2H_4O_3N_2$ (B) and with hydrogen in the presence of a catalyst C_2H_7N (C). With nitrous acid C gives C_2H_6O (D) which oxidises to $C_2H_4O_2$ (E). Identify the compounds A to E.

2. Derive the structure of a compound (A) from the following data :

(*i*) The compound contains only carbon, hydrogen and nitrogen. It gave the following results on analysis : C=61·02% ; H=15·25%.

(*ii*) By the reaction of *n*-amyl nitrite and hydrochloric acid at 273K, 5·9 g of the substance liberated 2·8 g of nitrogen at NTP.

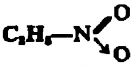
(*iii*) 5·9 g of the compound formed a salt with 3·65 g of hydrochloric acid.
(*Lucknow B.Sc. 1966*)

3. An aliphatic organic compound A gave the following results : C=61·01%, H=15·25%, N=23·74%.

On treatment with nitrous acid A gave another product B which contains C=60·00%, H=13·33% and no nitrogen. B on careful oxidation gave a compound C which gave iodoform on treatment with iodine and alkali and had mol wt 58. What structural formula would you assign to A, B and C ? Explain the above reactions with equations. (*Gwalior B.Sc. 1965*)

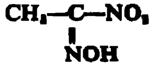
4. An organic compound containing C, H and N only was found to contain C=61·03, N=23·71%. Its V.D.=29·5. On treatment with nitrous acid it gave out nitrogen. Identify the compound and explain the reactions.
(*Agra B.Sc. 1963 Supp.*)

ANSWERS

1. A is 

$C_2H_5-N\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix}$

(Nitroethane)

B is 

$CH_3-\underset{\underset{NOH}{\|}}{C}-NO_2$

(*Nitrolic acid*)

C is $C_2H_5NH_2$ (*Ethylamine*) ; D is C_2H_5OH (*Ethanol*) ;

E is CH_3COOH (*Acetic acid*).

2. $CH_3.CH_2.CH_2NH_2$ *n*-Propylamine or $(CH_3)_2CH.NH$ Isopropylamine

3.

$\begin{smallmatrix}CH_3\\ CH_3\end{smallmatrix}\!\!>CHNH_2$;

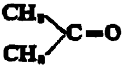
Isopropylamine

(A)

$\begin{smallmatrix}CH_3\\ CH_3\end{smallmatrix}\!\!>CHOH$;

Isopropyl alcohol

(B)



$\begin{smallmatrix}CH_3\\ CH_3\end{smallmatrix}\!\!>C=O$

Acetone

(C)

4. $CH_3.CH_2.CH_2NH_2$ *n*-Propylamine or $(CH_3)_2CH.NH_2$ Isopropylamine

$$C_3H_7NH_2+HONO \longrightarrow C_3H_7OH+N_2+H_2O$$

28

Cyanogen Compounds

1. Introductory.—The monovalent group $-C \equiv N$ was discovered by Gay Lussac in 1815 and named *cyanogen* as this group was present in Prussian blue (*cyanogen*=blue compound forming). Compounds containing this group are called cyanogen compounds and many of these have proved to be important synthetic reagents.

2. Hydrocyanic acid, Hydrogen Cyanide (*Prussic acid*), HCN.—It was discovered by Scheele (1782) who got it by the hydrolysis of amygdalin, glucoside present in bitter almonds.

$$\underset{\text{Amygdalin}}{C_{20}H_{27}O_{11}N}+2H_2O \xrightarrow{\text{Acid}} HCN+\underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

Hydrogen cyanide occurs in leaves of certain plants such as *laurel*.

Preparation. (1) It is *prepared in the laboratory by heating sodium cyanide with dilute sulphuric acid.* The gas is dried over anhydrous calcium chloride.

$$NaCN+H_2SO_4 \longrightarrow HCN+NaHSO_4$$

(2) It is **prepared industrially** by the following methods :

(*i*) *By passing a mixture of methane, ammonia and oxygen over heated platinum gauze (catalyst) at 1270K.*

$$2CH_4 + 2NH_3+3O_2 \longrightarrow 2HCN+6H_2O$$

(*ii*) *By passing a mixture of carbon monoxide and ammonia over heated alumina (catalyst) at 770-970K.*

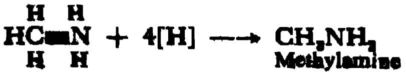
$$CO + NH_3 \longrightarrow HCN + H_2O$$

Properties : Physical. It is a colourless, volatile liquid (b.p. 299K) miscible with water, alcohol and ether in all proportions. It smells like bitter almonds and is a deadly poison. Even minute doses prove fatal.

Chemical. (*i*) HYDROLYSIS. It hydrolyses slowly in aqueous solution and more rapidly in acidic solution to give formamide and ammonium formate.

$$HCN \xrightarrow{H_2O} \underset{\text{Formamide}}{HCONH_2} \xrightarrow{H_2O} \underset{\text{Amm. formate}}{HCOONH_4}$$

(*ii*) REDUCTION. With nascent hydrogen, hydrocyanic acid is reduced to methylamine.



$$H\overset{H}{\underset{H}{C}}\equiv\overset{H}{\underset{H}{N}} + 4[H] \longrightarrow \underset{\text{Methylamine}}{CH_3NH_2}$$

Uses. Hydrogen cyanide finds use in organic synthesis, *e.g.*, in the preparation of cyanohydrins and aromatic aldehydes. It is also used in killing insects and rats.

Structure of Hydrocyanic Acid. (*i*) Hydrogen cyanide gives rise to two series of alkyl derivatives—alkyl cyanides and alkyl isocyanides. It is, therefore, believed to exist in two tautomeric forms as given below :

$$\begin{array}{ccc} H—C\equiv N & \rightleftharpoons & C\overset{\leftarrow}{=}N—H \\ \text{Hydrogen cyanide} & & \text{Hydrogen isocyanide} \\ \text{Gives}\downarrow\text{alkyl deriv.} & & \text{Gives}\downarrow\text{alkyl deriv} \\ R—C\equiv N & & R—N\overset{\rightarrow}{=}C \\ \text{Alkyl cyanide} & & \text{Alkyl isocyanide} \end{array}$$

(*ii*) The belief, however, cannot be regarded as very satisfactory as all reactions of the acid, *e.g.*, hydrolysis to formamide and formic acid indicate the structure H—C≡N. Moreover, existence of cyanides and isocyanides can be explained without assuming tautomeric structure of the acid as follows :

Potassium cyanide is an electrovalent compound, $K^+[:C\equiv N:]^-$ in which both carbon and nitrogen atoms have a lone pair. Out of these two, lone pair of carbon is more reactive and the potential alkyl carbonium ion preferentially attacks the carbon atom thereby producing alkyl cyanide.

$$[:C\equiv N:]^-K^+ + R—I \longrightarrow \underset{\text{Alkyl cyanide}}{R—C\equiv N:} + KI$$

On the other hand, silver cyanide, Ag—C≡N : is a covalent compound. When treated with an alkyl halide, the potential alkyl carbonium ion is driven to the nitrogen to yield mainly alkyl isocyanide.

$$Ag—C\equiv N: + R—I \longrightarrow [Ag—C\equiv N—R]^+I^- \xrightarrow{-AgI} \underset{\text{Alkyl isocyanide}}{R—N\overset{\rightarrow}{=}C:}$$

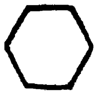
3. Alkyl Cyanides, R—C≡N.

Nomenclature. These are named either as *alkyl cyanides* or as the *nitriles* of the acids which they produce on hydrolysis. The suffix *-ic acid* of the trivial name is replaced by *-onitrile, e.g.*,

Formula		*Corresponding acid*	*Name*
HCN	$\xrightarrow{H_2O}$	HCOOH (*Formic acid*)	Hydrogen cyanide or Formonitrile
$CH_3.CN$	$\xrightarrow{H_2O}$	CH_3COOH (*Acetic acid*)	Methyl cyanide or Acetonitrile
$C_2H_5.CN$	$\xrightarrow{H_2O}$	C_2H_5COOH (*Propionic acid*)	Ethyl cyanide or Propiononitrile

In the IUPAC system acyclic cyanides are preferably named substitutively by adding the suffix nitrile to the name of the corresponding hydrocarbon. For example, CH_3CN is ethanenitrile

C_2H_5CN is propanenitrile and $CH_3CH{=}CHCN$ is 2-Butenenitrile. Cyclic nitriles are named by adding the suffix carbonitrile to the name of the ring system to which CN group is attached. For example


—CN is cyclohexanecarbonitrile

As alternatives **trivial names** may be used for nitriles in instances where the corresponding acid has an acceptable trivial name, *e g*, acetonitrile for CH_3CN and succinonitrile for

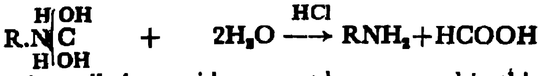
$$NC{-}CH_2{-}CH_2{-}CN.$$

Names such as succinonitrile imply that all COOH groups have been changed to CN groups.

Preparation. (*i*) *By heating an alkyl iodide with potassium cyanide in aqueous ethanolic solution.* The isocyanide is also obtained though in small amount.

$$R\underline{|I + K|}CN \longrightarrow R.CN+KI \qquad (g.)$$

The isocyanide may be removed by shaking with dilute hydrochloric acid which hydrolyses the isocyanide and does not affect the cyanide.



$$R.N\begin{smallmatrix}H|OH\\ C\\ H|OH\end{smallmatrix} \quad + \quad 2H_2O \xrightarrow{HCl} RNH_2+HCOOH$$

Tertiary alkyl cyanides cannot be prepared in this way as the tertiary alkyl halides readily eliminate a molecule of halogen acid and yield olefins on being heated with potassium cyanide.

(*ii*) Cyanides, particularly the lower members, may also be readily obtained *by warming potassium alkyl sulphate with potassium cyanide.* A small amount of isocyanide is also obtained.

$$R{-}\boxed{SO_4{-}K+K}CN \longrightarrow R{-}CN+K_2SO_4 \qquad (g.\text{-}v.g.)$$

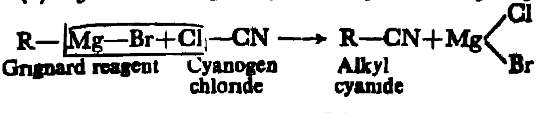
(*iii*) *By the dehydration of acid amides with phosphorus pentoxide.* High molecular weight acid amides are dehydrated by heat alone.

$$\underset{\text{Acid amide}}{RCO.NH_2} \xrightarrow[-H_2O]{P_4O_{10}} \underset{\text{Alkyl cyanide}}{RCN}$$

(*iv*) *By the dehydration of aldoximes with phosphorus pentoxide or better with acetic anhydride.*

$$RCH{=}NOH \xrightarrow[-H_2O]{(CH_3CO)_2O} R.CN \qquad (g.)$$

(*v*) *By the action of Grignard reagent with cyanogen chloride.*



$$\underset{\text{Grignard reagent}}{R{-}\boxed{Mg{-}Br+Cl}}\underset{\substack{\text{Cyanogen}\\ \text{chloride}}}{{-}CN} \longrightarrow \underset{\substack{\text{Alkyl}\\ \text{cyanide}}}{R{-}CN}+Mg\begin{smallmatrix}Cl\\ Br\end{smallmatrix}$$

The method is very useful for preparing tertiary alkyl cyanides.

(*vi*) *By passing mixture of carboxylic acid and ammonia over heated alumina at 770K*—(**Industrial Method**). Possibly ammonium

salt is formed as an intermediate product which is catalytically dehydrated to the cyanide.

$$RCOOH \xrightarrow{NH_3} RCOONH_4 \xrightarrow[-H_2O]{Al_2O_3} RCONH_2 \xrightarrow[-H_2O]{Al_2O_3} RCN$$

Properties : **Physical.** Alkyl cyanides are neutral substances with fairly pleasant smell. Lower members are liquids which are soluble in water. The solubility, however, diminishes as the molecular weight increases. They are all readily soluble in organic solvents. These are not as poisonous as hydrogen cyanide.

Chemical. (*i*) *Hydrolysis.* The alkyl cyanides are hydrolysed to acids by acids or alkalis. Amides are formed as intermediate products.

$$\underset{\text{Alkyl cyanide}}{R{-}C{\equiv}N} \xrightarrow{H_2O} \underset{\text{Acid amide}}{RCONH_2} \xrightarrow{H_2O} \underset{\text{Acid}}{RCOOH}+NH_3 \quad (g.\text{-}v.g.)$$

Partial hydrolysis of alkyl cyanide to acid amide may be effected with alkaline hydrogen peroxide or moderately concentrated sulphuric acid.

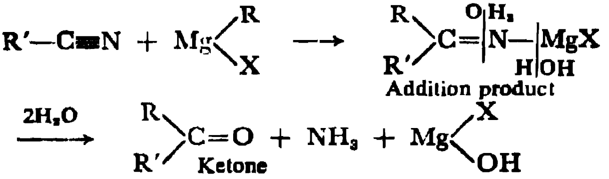
(*ii*) *Reduction.* Reduction of alkyl cyanide with nascent hydrogen (from sodium and alcohol) or catalytic reduction produces primary amine.

$$\underset{\text{Alkyl cyanide}}{RC{\equiv}N} + 4[H] \xrightarrow{Na/C_2H_5OH} \underset{\text{Primary amine}}{RCH_2NH_2}$$

(*iii*) *Stephen's reaction.* Alkyl cyanides undergo Stephen's reaction to produce aldehydes.

$$R.C{\equiv}N \xrightarrow[+HCl]{SnCl_2} R.CH{=}NH.HCl \xrightarrow[-NH_4Cl]{H_2O} RCHO$$

(*iv*) *With Grignard reagent.* They react with Grignard reagent and the addition products on hydrolysis yield ketones.



4. Alkyl Isocyanides, Isonitriles or Carbylamines.

Nomenclature. These are named either as the alkylisocyanides or putting the prefix *iso-* before the name of the isomeric carbonitrile. Their IUPAC names are derived substitutively. As a substituent NC is termed carbylamine. Thus CH_3NC is carbylaminomethane and so on.

Formula	*Isomeric nitrile*	*Common name*	*IUPAC name*
CH_3NC	CH_3CN (*Acetonitrile*)	Methylisocyanide or Aceto isonitrile	Carbylaminomethane
C_2H_5NC	C_2H_5CN (*Propiononitrile*)	Ethyl isocyanide or Propionoisonitrile	Carbylaminoethane
C_3H_7NC	C_3H_7CN (*Butyronitrile*)	Propyl isocyanide or Butyroisonitrile	Carbylaminopropane

According to the IUPAC recommendations Radicofunctional names such as methyl isocyanide or class name isonitrile is also not recommended. Older names based on carbylamine have largely disappeared and should not be revived.

Preparation. (*i*) *By heating an alkyl iodide with silver cyanide in aqueous ethanolic solution.* A small amount of alkyl cyanide is also obtained.

$$RI + AgCN \longrightarrow RNC + AgI$$

(*ii*) *By heating a primary amine with chloroform and alcoholic potash.* The isocyanide obtained is free from cyanide.

$$RN|\overline{H_2 + \underbrace{Cl_3H|C}_{\text{Chloroform}}} + \underset{\text{(Alcoholic)}}{3KOH} \longrightarrow R.NC + 3KCl + 3H_2O$$

Properties : Physical. Isocyanides are colourless mobile liquids with intolerable smell. They are more poisonous and have lower boiling points than the isomeric cyanides. They are not very soluble in water.

Chemical. (*i*) *Hydrolysis.* On hydrolysis with dilute acids, alkyl isocyanides yield an amine and formic acid. *These are not hydrolysed by alkalis.*

$$\begin{array}{r|l} H & OH \\ H & OH \\ R.N & C \end{array} + 2H_2O \xrightarrow{\text{acid}} RNH_2 + HCOOH$$

(*ii*) *Reduction.* On catalytic reduction or with nascent hydrogen, alkyl isocyanides yield secondary amines.

$$R.NC + 4[H] \longrightarrow R.NH.CH_3$$

(*iii*) *Action of Heat.* Alkyl isocyanides, when heated for a long time, rearrange to give cyanides.

$$R.NC \longrightarrow R.CN$$

(*iv*) *Addition of halogen, sulphur or oxygen.* Alkyl isocyanides add one molecule of a halogen to give alkyliminocarbonyl halides.

$$R.NC + X_2 \longrightarrow RN{=}CX_2$$

With sulphur they form alkyl isothiocyanates.

$$R.NC + S \longrightarrow RN{=}CS$$

These are readily oxidised by mercuric oxide to produce alkyl isocyanates.

$$R.NC + HgO \longrightarrow RNCO + Hg$$

5. Distinguishing Tests of Ethyl Cyanide and Ethyl Isocyanide.—Various tests employed for distinguishing one from the other are summarised in the table below :

Test	Ethyl cyanide	Ethyl isocyanide
1. Smell	Strong but not unpleasant.	Extremely unpleasant.
2. B.P.	344K.	351K
3. Solubility in water	Soluble.	Sparingly soluble
4. Hydrolysis with acid	Gives propionic acid. *(Similar with alkalis)* $C_2H_5CN+2H_2O=C_2H_5COOH+NH_3$	Gives ethylamine. *(Stable towards alkalis)* $C_2H_5NC+2H_2O=C_2H_5NH_2+HCOOH$
5 Reduction	Gives propylamine with sodium + alcohol. $C_2H_5CN+4H=C_2H_5CH_2NH_2$	Gives ethylmethylamine (*secondary*) on catalytic hydrogenation. $C_2H_5NC+2H_2=C_2H_5NH.CH_3$

6. Cyanogen (Ethanedinitrile or oxalonitrile), C_2N_2.—It may be prepared—

(*i*) *By heating cyanides of mercury or silver.*

$$Hg(CN)_2 \longrightarrow C_2N_2 + Hg$$

(*ii*) *By adding sodium cyanide solution to copper sulphate solution and heating.*

$$2CuSO_4+4NaCN \longrightarrow \underset{\substack{\text{Cuprous}\\\text{cyanide}}}{2CuCN} + C_2N_2+2Na_2SO_4$$

(*iii*) *By dehydration of oxamide with phosphorus pentoxide.*

$$\underset{\text{Oxamide}}{\begin{array}{c}CONH_2\\|\\CONH_2\end{array}} \xrightarrow[-2H_2O]{P_4O_{10}} \underset{\text{Cyanogen}}{\begin{array}{c}CN\\|\\CN\end{array}}$$

It is a colourless, poisonous gas (b.p. —252K), very soluble in water. It is combustible and burns with a violet flame to give carbon dioxide and nitrogen.

$$C_2N_2 + 2O_2 \longrightarrow 2CO_2 + N_2$$

7. Cyanogen Chloride, Cl—CN.—It is prepared by passing chlorine into a cooled solution of sodium cyanide.

$$NaCN+Cl_2 \longrightarrow Cl—CN+NaCl$$

It is a colourless, poisonous gas (b.p. 285K), very soluble in water, alcohol and ether.

8. Cyanic Acid.—It is believed to be a tautomeric mixture of cyanic acid and isocyanic acid.

$$\underset{\text{Cyanic acid}}{H—O—C\equiv N} \rightleftharpoons \underset{\text{Isocyanic acid}}{O=C=N—H}$$

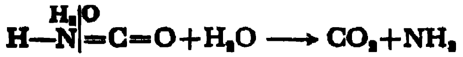
Out of these two acids, derivatives of only isocyanic acid have been obtained, *e.g.*, potassium isocyanate, KNCO and alkyl isoyanates, RNCO.

Preparation. Urea on distillation gives cyanuric acid which decomposes on heating to give cyanic acid vapours which are condensed below 273K.

$$\underset{\text{Urea}}{3CO(NH_2)_2} \xrightarrow[-3NH_3]{\text{distil}} \underset{\text{Cyanuric acid}}{(HOCN)_3} \xrightarrow{\text{Heat}} \underset{\text{Cyanic acid}}{3HOCN}$$

Properties. It is a colourless, volatile, strongly acidic liquid. Above 273K it readily polymerises to cyanuric acid.

In aqueous solution it gives carbon dioxide and ammonia due to hydrolysis.



$$H-\overset{H_2|O}{N}\boxed{=}C=O+H_2O \longrightarrow CO_2+NH_3$$

9. Alkyl Isocyanates, R—N=C=O.

Preparation. Alkyl isocyanates can be prepared—

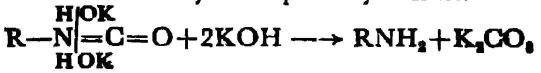
(*i*) *By heating alkyl iodides with silver or potassium isocyanates.*

$$C_2H_5\boxed{I \quad + \quad Ag}NCO \longrightarrow \underset{\text{Ethyl isocyanate}}{C_2H_5NCO} + AgI$$

(*ii*) *By the action of carbonyl chloride on primary amines.*

$$RN\boxed{H_2 \quad + \quad Cl_2}C=O \longrightarrow \underset{\text{Alkyl isocyanate}}{R-N=C=O}+2HCl$$

Properties. These are colourless liquids with suffocating odours. They gradually polymerise to give cyanuric esters. On hydrolysis with alkalis they form primary amines.



$$R-\underset{H\,OK}{\overset{H|OK}{N}}\boxed{=}C=O+2KOH \longrightarrow RNH_2+K_2CO_3$$

They react with alcohols to give N-substituted urethans which are well-defined crystalline solids and are used to characterise alcohols.

$$RNCO \quad + \quad R'OH \longrightarrow \underset{\text{N-substituted urethan}}{RNH.COOR'}$$

With ammonia they give substituted ureas.

$$R-N=C=O + HNH_2 \longrightarrow \underset{\text{Substituted urea}}{RNH.CO.NH_2}$$

QUESTIONS

Essay Type :

1. (*a*) How is hydrocyanic acid prepared ? What are its important properties ? Describe the action of hydrolysing and reducing agents on it.

(*b*) Describe the importance of hydrocyanic acid in organic chemistry for synthesis purposes.

2. How are cyanides and isocyanides prepared ? What are their properties and how are they distinguished from one another ?

3. How is acetonitrile prepared ? What are its important properties ?

4. Discuss critically the structural formulae of alkyl cyanides and alkyl isocyanides. How can these classes of compounds be prepared and distinguished ?

5. Explain by examples the isomerism of carbylamines and nitriles. How is each class of these prepared ? How can the formulae assigned to each be proved to be correct ? Give equations.

Short Answer Type :

Explain how you would proceed to distinguish between :

1. Methyl cyanide and Methyl isocyanide.
2. Ethyl cyanide and Ethyl isocyanide.
3. Cyanides and Isocyanides. (*Rajasthan B.Sc. 1971*)

4. Give electronic mechanism for the reaction of ethyl iodide with (*i*) KCN and (*ii*) AgCN.

5. Write equations for the reactions, if any, between :

(1) Alkyl cyanide on (*i*) Hydrolysis ; (*ii*) Reduction ; (*iii*) Stephen's reaction ; (*iv*) with RMgX.

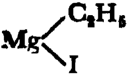
(2) Alkyl isocyanide (*i*) on hydrolysis ; (*ii*) on reduction ; (*iii*) on heating ; (*iv*) with halogen, sulphur or HgO.

6. Give the preparation and properties of (*a*) cyanogen ; (*b*) cyanic acid ; (*c*) Alkyl isocyanates.

29

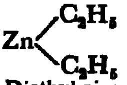
Organometallic Compounds

1. Introduction.—Organic compounds in which a metal is directly linked to carbon are termed *organometallic compounds.* For example,



$Mg(C_2H_5)I$

Ethylmagnesium iodide



$Zn(C_2H_5)_2$

Diethyl zinc

$Pb(C_2H_5)_4$

Tetraethyllead

These may be largely ionic or largely covalent. The ionic character of the carbon-metal bond depends on the nature of the metal. It decreases in the order given below :

$$Na > Li > Mg > Al > Zn > Cd > Hg$$

Thus organometallic compounds of alkali and alkaline earth metals consist of ions or ion pairs.

$\overset{-}{R}\overset{+}{Na}$	$\overset{-}{R}\overset{+2}{Mg}\overset{-}{X}$	$\overset{-}{C_6H_5}\overset{+}{Li}$
Alkyl sodium	Alkylmagnesium halide *(Grignard reagent)*	Phenyllithium
$R-C\equiv\overset{-}{C}\overset{+}{Na}$	$\overset{-}{R}\overset{+2}{Zn}\overset{-}{R}$	
Sodium alkynide	Dialkylzinc	

Lithium compounds are, however, fairly covalent and dissolve in hydrocarbon solvents. Some organometallic compounds of transition metals and group IV elements are covalent.

R_4Sn	R_4Si	$R-C\equiv C-Ag$	C_6H_5-HgCl
Tetra alkyltin	Tetra alkylsilane	Silver alkynide	Phenylmercuric chloride

Some organometallic compounds are prepared from the respective alkyl or aryl halides in hydrocarbon or ether solvents.

$$C_2H_5Br + Mg \longrightarrow C_2H_5MgBr$$
$$CH_3I + Zn \longrightarrow CH_3ZnI$$
$$C_6H_5Br + 2Li \longrightarrow C_6H_5Li + LiBr$$

Some hydrocarbons are sufficiently acidic to react with the metals directly.

$$R-C\equiv C-H + Na \xrightarrow{370K} R-C\equiv C-Na + \tfrac{1}{2}H_2$$

Most widely studied and most useful organometallic compounds are those of magnesium. Recently lithium compounds are becoming increasingly important in organic synthesis.

Organometallic compounds are mostly colourless, mobile liquids having low boiling points and are generally very unstable. A number of these burn violently in air and are readily decomposed by water and alcohol.

ORGANOMAGNESIUM COMPOUNDS

2. The Grignard Reagents.—The alkylmagnesium halides, R—Mg—X were introduced by the French chemist, Victor Grignard, in 1900 and are termed Grignard reagents. These are extremely valuable synthetic reagents and are being used on a large scale at present.

Preparation. A Grignard reagent is prepared in the laboratory by the interaction of dry magnesium turnings with alkyl halide in presence of dry alcohol-free ether.

$$RX + Mg \longrightarrow RMgX \qquad (v.g.\text{-}ex.)$$

It has been found that for a given alkyl radical the ease of formation of a Grignard reagent is

Iodide>Bromide>Chloride.

Similarly for a given halogen atom, the ease of formation is greater with smaller alkyl group than with bigger ones, *e.g.*,

$$CH_3I > C_2H_5I > C_3H_7I.$$

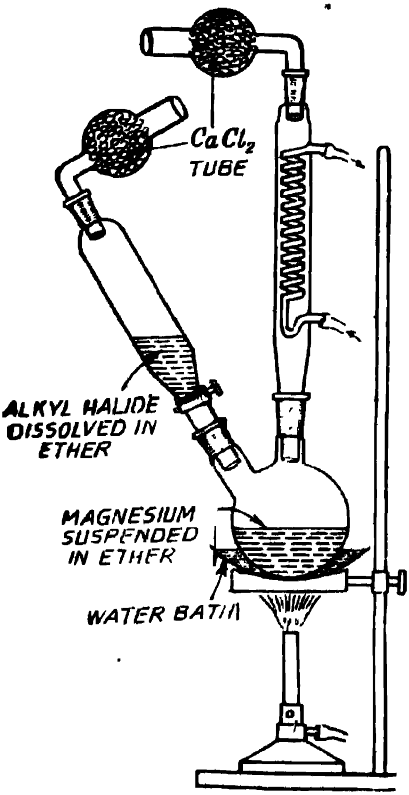


Fig. 29 1—Preparation of Grignard reagent.

Since tertiary alkyl iodides are readily decomposed to yield olefins, tertiary alkyl chlorides are used in their place.

Experiment. Clean magnesium turnings (1 g atom) with 5-10 times their weight of dry alcohol-free ether are taken in a two-necked round-bottom flask. The flask is fitted with a reflux condenser carrying calcium chloride tube at its upper end in one neck and a dropping funnel carrying a calcium chloride tube at its upper end in the other neck. The alkyl halide (*1 mole*) dissolved in ether is taken in the dropping funnel and slowly dropped in the flask.

It is usually necessary to warm the mixture or add flakes of iodine (*catalyst*) to start the reaction. Once the reaction starts, it often becomes vigorous and it is necessary to cool the mixture to prevent it from becoming violent.

A clear solution of Grignard reagent is obtained after the reaction is complete. This is used as such in all reactions and never isolated.

Precautions. (*i*) As a slight trace of moisture will prevent the reaction, the reagents used should be pure and dry. These must be kept away from the effect of moisture.

(*ii*) Ether should be washed with water to free it from alcohol and dried over anhydrous calcium chloride for 2-3 days to remove alcohol and moisture. It should be finally distilled over sodium and P_4O_{10} to remove last traces of water.

Victor Grignard (1871-1935)—French chemist ; won Nobel Prize in Chemistry in 1912 for his contribution to synthetic chemistry principally on the usefulness of the reaction which takes his name.

(*iii*) Magnesium turnings should be treated with ether to remove grease and then dilute hydrochloric acid to remove oxide film. They should be finally dried in an oven at 380-390K.

(*iv*) The alkyl halides should be dried by distilling over phosphorus pentaoxide.

(*v*) The apparatus—flask, condenser and funnel—should be completely dry.

3. Structure of the Grignard Reagents.—Structure of Grignard reagent in ethereal solution has been the subject of much research and many formulae have been proposed. Jolibois (1912) suggested that it was the loose molecular complex $R_2Mg.MgX_2$, whereas Schlenk (1929) suggested the following equilibrium :

$$2RMgX \rightleftharpoons R_2Mg+MgX_2.$$

They found that a mixture of dialkylmagnesium and magnesium halide in equivalent proportions behaved exactly as a Grignard reagent. This, however, can be explained by the dissociation of the Jolibois complex, $R_2Mg.MgX_2$

$$R_2Mg.MgX_2 \rightleftharpoons R_2Mg+MgX_2$$

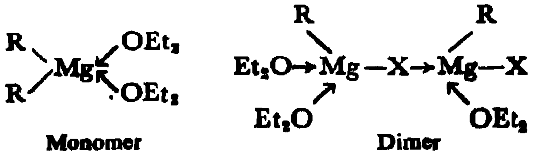
According to Ubbelohde (1955) RMgX is dimerised and solvated in ether and the following equilibria are possible.

$$R_2Mg.MgX_2 \overset{A}{\rightleftharpoons} R_2Mg+MgX_2 \overset{B}{\rightleftharpoons} 2RMgX$$

According to Ashby (1967), composition of Grignard reagent in ether is as given by the following equilibrium :

$$\text{etc.} \rightleftharpoons \text{Dimer} \rightleftharpoons R_2Mg + MgX_2 \rightleftharpoons 2RMgX \rightleftharpoons \text{Dimer} \rightleftharpoons \text{etc.}$$

The association increases with concentration and is extensive at 0·3 M and above. The monomer and dimer coordinate with ether molecules as shown below :



Monomer (dietherate) Dimer (trietherate)

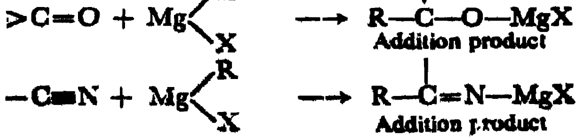
In this book, the formula RMgX will be used to designate a Grignard reagent.

4. Properties : Physical. Grignard reagents are colourless, nonvolatile solids. They are, however, seldom prepared in the solid state. They do not ignite in contact with air.

Chemical. (*i*) *Addition reactions with compounds containing groups* :

$$>C=O, \quad -C\equiv N \quad \text{or} \quad >C=S$$

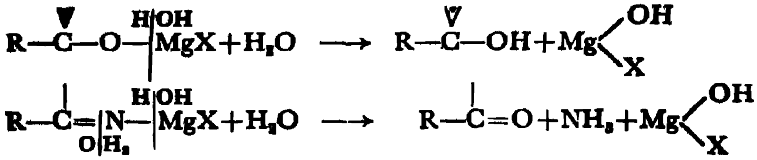
In each case the alkyl group attaches to the carbon atom and the fragment MgX to the oxygen or nitrogen atom.



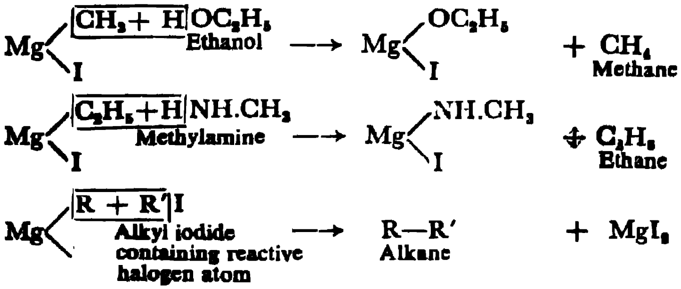
Addition product

Addition product

The addition products decompose with water or dilute acid and yields of the products are usually *g.-v.g.*


R—C—O—MgX+H₂O ⟶ R—C—OH+Mg(OH)X
R—C=N—MgX+H₂O ⟶ R—C=O+NH₃+Mg(OH)X

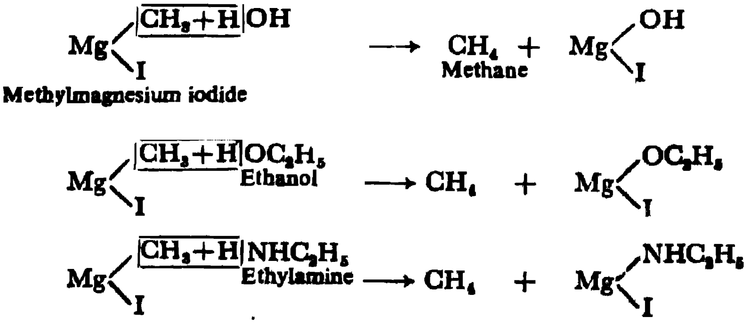
(*ii*) ***Double decomposition with compounds containing active hydrogen atom or reactive halogen atom.*** Active hydrogen atom is one joined to an oxygen, nitrogen or sulphur atom. As a result of double decomposition the alkyl group combines with the active hydrogen to yield alkanes.



Experiments have shown that *reactive halogen atom reacts very much faster than other groups* ($>C=O$; —C≡N, etc.).

5. Synthetic Uses of Grignard Reagents.—Grignard reagents are one of the most reactive compounds known to an organic chemist. These are used for the synthesis of a very large number of organic compounds given below :

(1) **Alkanes.** Grignard reagents undergo double decomposition with water, alcohols and amines (compounds containing active hydrogen) to produce alkanes.



These reactions are quantitative and methane liberated can be measured. This gives us a method for the estimation of OH and amino groups.

Higher alkanes are obtained when Grignard reagent is treated with an alkyl halide (*compound containing reactive halogen atom*).

$$CH_3\boxed{MgI + I}C_2H_5 \longrightarrow \underset{\text{Propane}}{CH_3.C_2H_5} + MgI_2$$

(2) **Alkenes.** These are obtained by the action of unsaturated halides on Grignard reagent.

$$CH_3\boxed{MgBr + Br}\underset{\text{Allyl bromide}}{CH_2.CH{=}CH_2} \longrightarrow \underset{\text{1-Butene}}{CH_3.CH_2.CH{=}CH_2} + MgBr_2$$

Alkenes are also obtained from tertiary alcohols which are formed by the interaction of a ketone and a Grignard reagent [*see property* (6)].

$$\underset{\textit{tert.}\text{ Butyl alcohol}}{(CH_3)_3COH} \xrightarrow{\text{Heat}} \underset{\text{Isobutene}}{(CH_3)_2C{=}CH_2} + H_2O$$

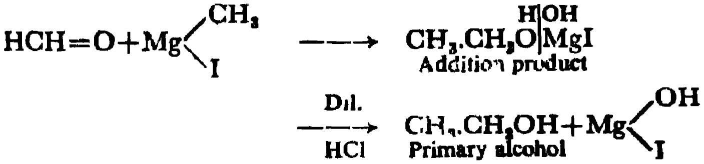
(3) **Alkynes.** Lower alkynes with active hydrogen atom undergo double decomposition with Grignard reagents. The product reacts with an alkyl halide to give higher alkyne.

$$\underset{\text{Propyne}}{CH_3.C{\equiv}C}\boxed{H + CH_3}MgI \xrightarrow[\text{decomposition}]{\text{Double}} CH_3C{\equiv}C{-}MgI + CH_4$$

$$CH_3.C{\equiv}C.\boxed{MgI + I}CH_3 \longrightarrow \underset{\text{2-Butyne}}{CH_3C{\equiv}C.CH_3} + MgI_2$$

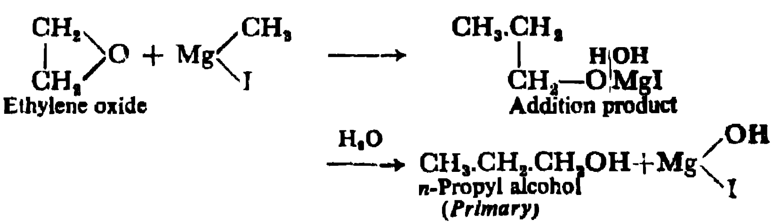
(4) **Primary Alcohols.**

(*i*) *By the action of Grignard reagent on formaldehyde and hydrolysis of the product with dilute hydrochloric acid.*



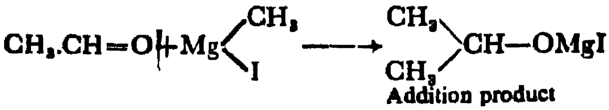
$$HCH{=}O + Mg\begin{smallmatrix}CH_3\\I\end{smallmatrix} \longrightarrow \underset{\text{Addition product}}{CH_3.CH_2O\overset{H\,|\,OH}{MgI}} \xrightarrow[\text{HCl}]{\text{Dil.}} \underset{\text{Primary alcohol}}{CH_3.CH_2OH} + Mg\begin{smallmatrix}OH\\I\end{smallmatrix}$$

(*ii*) *By the action of Grignard reagent on ethylene oxide.*

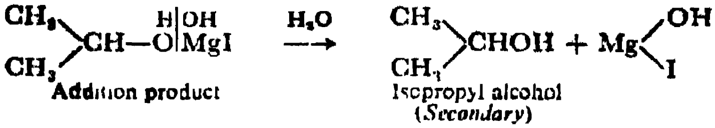


$$\underset{\text{Ethylene oxide}}{\begin{matrix}CH_2\\|\\CH_2\end{matrix}\!>O} + Mg\begin{smallmatrix}CH_3\\I\end{smallmatrix} \longrightarrow \underset{\text{Addition product}}{\begin{matrix}CH_3.CH_2\\|\\CH_2{-}O\overset{H\,|\,OH}{MgI}\end{matrix}} \xrightarrow{H_2O} \underset{\substack{n\text{-Propyl alcohol}\\(\textit{Primary})}}{CH_3.CH_2.CH_2OH} + Mg\begin{smallmatrix}OH\\I\end{smallmatrix}$$

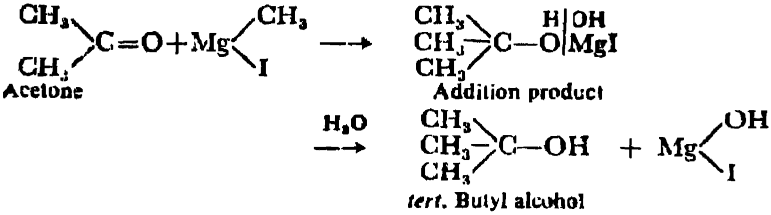
(5) **Secondary Alcohols.** These are prepared *by the action of Grignard reagent on aldehydes other than formaldehyde.*



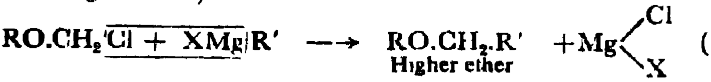
$$CH_3.CH{=}O + Mg\begin{smallmatrix}CH_3\\I\end{smallmatrix} \longrightarrow \underset{\text{Addition product}}{\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}\!>CH{-}OMgI}$$



(6) **Tertiary Alcohols.** These are prepared *by the action of Grignard reagent on ketones.*



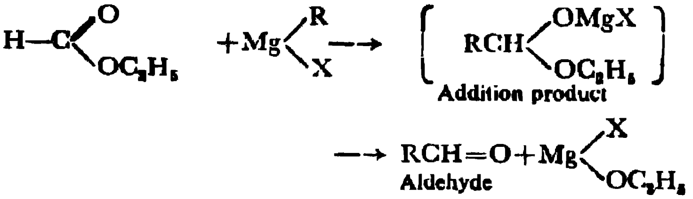
(7) **Ethers.** Higher ethers are prepared *by the action of Grignard reagent on a monochloroether* (a compound containing reactive halogen atom).



(g.)

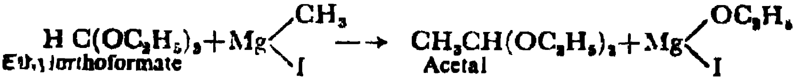
(8) **Aldehydes.** These are prepared by the action of Grignard reagent with—

(*i*) *Ethyl formate.*



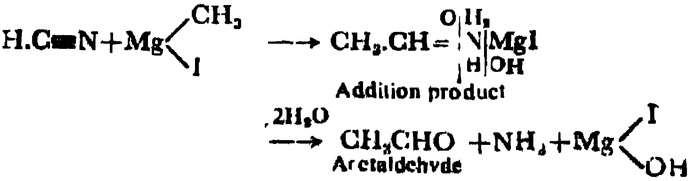
A secondary alcohol is obtained if Grignard reagent used is in excess. Aldehyde produced reacts further to give secondary alcohol.

(*ii*) *Ethyl orthoformate.* A better yield of aldehyde is obtained with this since the formation of secondary alcohol is prevented by the formation of an acetal.



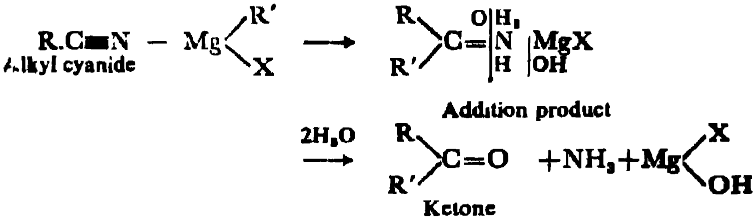
$$\underset{\text{Acetal}}{CH_3CH(OC_2H_5)_2} \xrightarrow{\text{Acid}} \underset{\text{Acetaldehyde}}{CH_3CHO} + 2C_2H_5OH$$

(*iii*) *Hydrogen cyanide.*



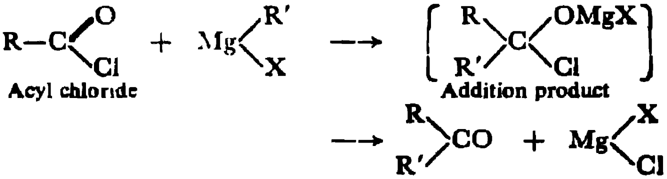
(9) **Ketones.** These are prepared—

(*i*) *By adding an alkyl cyanide to Grignard reagent and decomposing the addition product with dilute acid.*

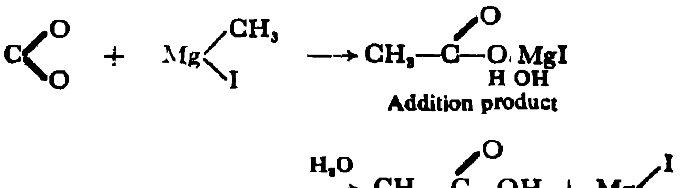


(*ii*) *With acid chlorides.* The reaction is quite rapid and some tertiary alcohol is also formed due to the action of Grignard reagent on ketone produced.

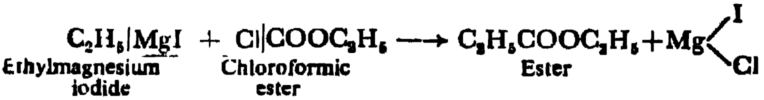
Mechanism of the reaction is not certain but it appears to be additive and not double decomposition.



(10) **Carboxylic Acids.** These are prepared by reacting Grignard reagent with solid carbon dioxide and decomposing the addition product with dilute acid.

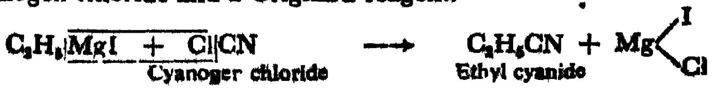


(11) **Esters.** An ester is produced when Grignard reagent (1 molecule) reacts with ethyl chloroformate (1 molecule).

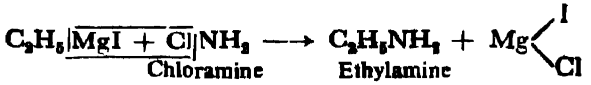


$$\underset{\text{Ethylmagnesium iodide}}{C_2H_5|MgI} + \underset{\text{Chloroformic ester}}{Cl|COOC_2H_5} \longrightarrow \underset{\text{Ester}}{C_2H_5COOC_2H_5} + Mg\begin{matrix} I \\ Cl \end{matrix}$$

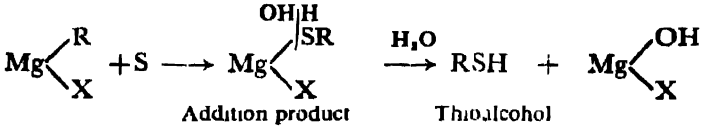
(12) **Alkyl Cyanides.** These are prepared by the interaction of cyanogen chloride and a Grignard reagent.



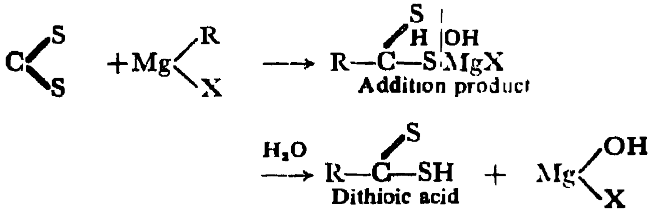
$$C_2H_5|MgI + \underset{\text{Cyanogen chloride}}{Cl|CN} \longrightarrow \underset{\text{Ethyl cyanide}}{C_2H_5CN} + Mg\begin{matrix} I \\ Cl \end{matrix}$$



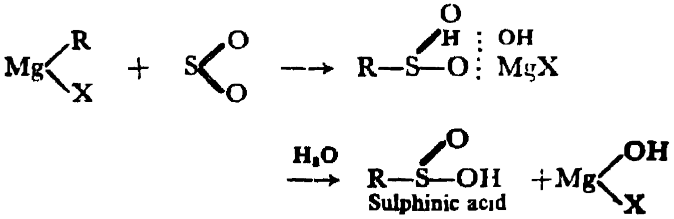
(13) **Thioalcohols.** This can be prepared by the action of sulphur on Grignard reagent and hydrolysis of the addition product



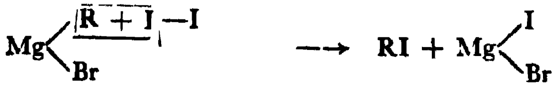
(14) **Dithioic Acids.** These may be prepared by the action of carbon disulphide on Grignard reagent (*cf.* carboxylic acids).



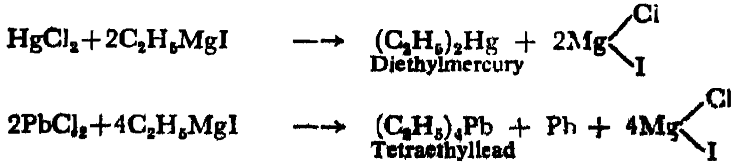
(15) **Sulphinic Acids.** These may be prepared by passing sulphur dioxide into a well-cooled solution of Grignard reagent when magnesium complex of a sulphinic acid is precipitated. This is hydrolysed to get the sulphinic acid.



(16) **Alkyl Iodides.** Alkyl iodides may be prepared by treating alkylmagnesium chlorides or bromide with iodine.



(17) **Organometallic Compounds.** Grignard reagents react with metal chlorides to give organometallic compounds.



6. Limitations of Grignard Synthesis.—The high reactivity of Grignard reagent makes it useful in organic synthesis.

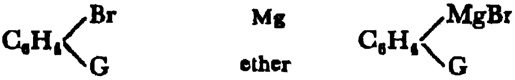
therefore, to be kept in mind while selecting the halide that is to become Grignard reagent and when we select the compound with which it is to react.

In the preparation of Grignard reagent we have learnt that the ether used as a solvent must be scrupulously dried and freed from alcohol. Apparatus and reagents should be perfectly dry and the reaction system must be protected from water vapour, carbon dioxide and oxygen of the air.

We cannot prepare a Grignard reagent from a compound which contains, in addition to halogen, some reactive group like —OH which will react rapidly with the Grignard reagent produced. For example, $HOCH_2.CH_2Br$ gives a Grignard reagent which reacts with the active —OH group in another molecule to give the unwanted product, $HOCH_2.CH_2$—H.

Similarly, aryl halides containing reactive substituents (*e.g.*, —COOH, —OH, —NH_2 and —SO_3H) in the benzene ring cannot be used since Grignard reagent obtained will at once react with the reactive group present in another molecule. Grignard reagent gives addition products with $>C=O$, —COOR and —C≡N groups. The nitro group oxidises a Grignard reagent. Hence none of these groups should be present in the nucleus.

Thus it turns out that only a few groups (*e.g.*, —R, —Ar, —OR and —Cl) may be present in the halide molecule from which we prepare a Grignard reagent.



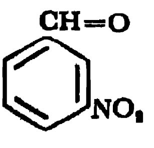
$$C_6H_4\begin{cases}Br\\G\end{cases}\xrightarrow[\text{ether}]{Mg}C_6H_4\begin{cases}MgBr\\G\end{cases}$$

Grignard reagent

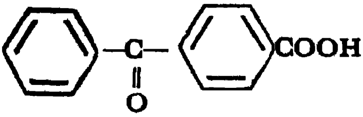
G should not be —COOH, —OH, —NH_2, —SO_3H, $>C=O$, —COOR, —C≡N, —NO_2 and many others.

G may, however, be R, Ar (aryl group), —OR, —Cl.

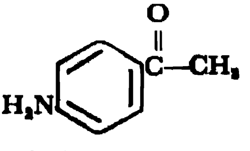
By the same token, the other compound with which a Grignard reagent is to react must not contain other groups that are reactive towards a Grignard reagent. For example, a Grignard reagent adds to a carbonyl group ($>C=O$) but it would be decomposed before it could add to the carbonyl group in the following compounds which contain the groups —NO_2, —NH_2 and —COOH respectively that are reactive towards the Grignard reagent.



m-Nitrobenzaldehyde



p-Benzoylbenzoic acid



p-Aminoacetophenone

Special precautions have to be taken while preparing compounds with the help of Grignard reagents. We should not only restrict our attention to the group we happen to be interested in, but also bear in mind the possible interference by the other functional groups present in the molecule.

Thus we find there are severe limitations on the use of Grignard reagent in organic synthesis but the number of acceptable combinations is so large that the Grignard reagent is one of the most valuable synthetic tools in the hands of the organic chemist.

ORGANOZINC COMPOUNDS

7. **Dialkylzincs.**—The dialkylzincs were the first organometallic compounds discovered by Frankland in 1849 while he was trying to prepare the ethyl radical by removing iodine from ethyl iodide by means of zinc.

Preparation. Dialkylzinc can be prepared by heating alkyl iodide with zinc in an atmosphere of carbon dioxide and distilling the product, alkylzinc iodide in an atmosphere of carbon dioxide.

$$RI + Zn \longrightarrow \underset{\text{Alkylzinc iodide}}{R{-}Zn{-}I}$$

$$2RZnI \longrightarrow \underset{\text{Dialkylzinc}}{R_2Zn} + ZnI_2$$

The yield of dialkylzinc may be increased by carrying out distillation in vacuo. The best yields of the compound are obtained by taking zinc-copper couple or zinc-copper alloy in place of zinc.

Dialkylzincs are colourless volatile liquids with unpleasant smell and low boiling points [$(CH_3)_2Zn$, 319K ; $(C_2H_5)_2Zn$, 391K]. They are spontaneously inflammable in air (hence the necessity of carbon dioxide atmosphere in their preparation). They burn the skin.

Their uses in Organic Synthesis. Dialkylzincs have been used in various synthetic reactions. Owing to the difficulty in handling them and because better synthetic reagents are known, their use is restricted to the following preparations :

(*i*) *Preparation of hydrocarbons containing quaternary carbon atom.* For example, neopentane is prepared by the action of dimethyl zinc on *tert.* butyl chloride.

$$\underset{\textit{tert. butyl chloride}}{(CH_3)_3CCl} + (CH_3)_2Zn \rightarrow \underset{\textit{neopentane}}{(CH_3)_4C} + CH_3ZnCl \qquad (\textit{f.-f.g.})$$

Dialkylzincs do not react with primary or secondary alkyl halides.

(*ii*) *Preparation of ketones.* Dialkylzincs react with acid chlorides to give ketones.

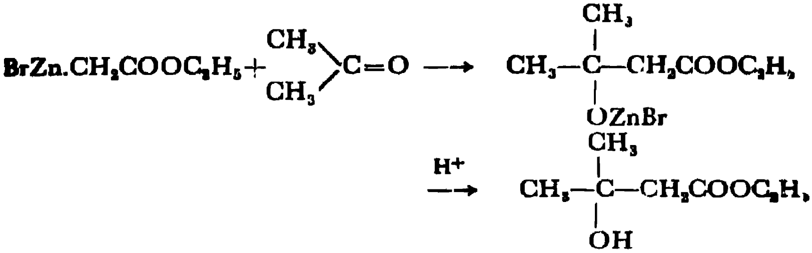
$$\underset{\text{Acyl chloride}}{R'COCl} + R_2Zn \rightarrow \underset{\text{Ketone}}{R'COR} + RZnCl \qquad (\textit{g.-v.g.})$$

Ketones are isolated in good yield because dialkylzincs react very slowly with them.

(*iii*) *Reformatsky reaction* (1887). It is the reaction in absolute ether between an α-bromo ester and a carbonyl compound (aldehyde, ketone or ester) in the presence of zinc to get a β-hydroxyester. Zinc is added to the mixture of bromoacid ester and carbonyl compound in absolute ether and then warmed.

The α-bromoester and zinc react in ether to yield an intermediate organozinc compound which then adds to the carbonyl group of the aldehyde and ketone.

$$\underset{\substack{\text{Ethyl bromoacetate}\\ (\alpha\text{-bromoester})}}{BrCH_2COOC_2H_5} \xrightarrow{Zn} \underset{\substack{\text{Intermediate organozinc}\\ \text{compound}}}{BrZnCH_2COOC_2H_5}$$



$$BrZn.CH_2COOC_2H_5 + \begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>C=O \longrightarrow CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle OZnBr}{C}}-CH_2COOC_2H_5$$

$$\xrightarrow{H^+} CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{C}}-CH_2COOC_2H_5$$

Ethyl β-hydroxyisovalerate

ORGANOLITHIUM COMPOUNDS

8. **Alkyllithiums.**—Organoalkali compounds—the alkyllithiums, the alkylsodiums and alkylpotassiums—have been prepared. These, like the organomagnesium derivatives, are very reactive and have been found to be more useful than the Grignard reagents for some syntheses. Alkyllithiums are briefly discussed below :

Preparation. (1) Some organolithium compounds can be prepared by heating an alkyl or an aryl halide in ether or benzene with metallic lithium, *e.g.*,

$$RX + 2Li \longrightarrow \underset{\text{Alkyllithium}}{RLi} + LiX$$

$$\underset{n\text{-Butyl chloride}}{CH_3.CH_2.CH_2.CH_2Cl} + 2Li \longrightarrow \underset{n\text{-Butyllithium}}{CH_3.CH_2.CH_2.CH_2Li} + LiC$$

Alkyl bromides and iodides usually undergo Wurtz reaction Alkyl chlorides, aryl bromides and aryl iodides give good yields o lithium compounds.

(2) *Halogen-metal exchange.* Many alkyllithiums can be prepared by an *exchange reaction* by heating a suitable alkyllithium (usually *n*-butyllithium) with an appropriate alkyl halide.

$$RLi + R'X \longrightarrow R'Li + RX$$

(R is usually *n*-butyl radical.)

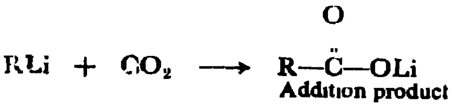
Properties. The alkyllithiums are either colourless liquids or solids with low melting points. They are insoluble covalent compounds which may have partial ionic character according to the nature of the alkyl group. Thus methyllithium is covalent while *n*-butyllithium has considerable degree of polarity (due to partial ionic character).

Alkyllithiums behave, generally, like Grignard reagents but are more reactive. A few examples of their reactions are given on the next page.

(1) $$\underset{n\text{-Butyllithium}}{C_4H_9Li} + H_2O \longrightarrow \underset{n\text{-Butane}}{C_4H_{10}} + LiOH$$

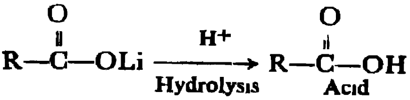
(2) $$3CH_3Li + \underset{\substack{\text{Auric}\\ \text{bromide}}}{AuBr_3} \longrightarrow \underset{\text{Trimethylgold}}{(CH_3)_3Au} + 3LiBr$$

(3) (a)



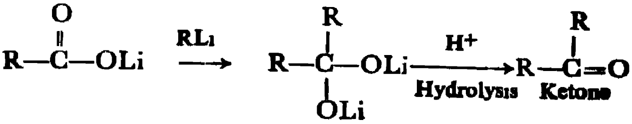
$$RLi + CO_2 \longrightarrow \underset{\text{Addition product}}{R—\overset{\overset{O}{\|}}{C}—OLi}$$

(b)



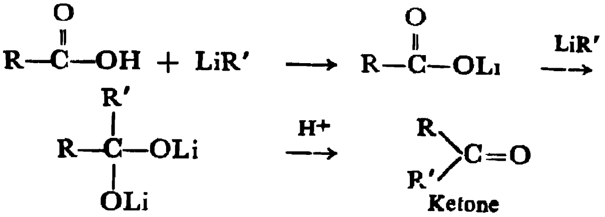
$$R—\overset{\overset{O}{\|}}{C}—OLi \xrightarrow[\text{Hydrolysis}]{H^+} \underset{\text{Acid}}{R—\overset{\overset{O}{\|}}{C}—OH}$$

(c)

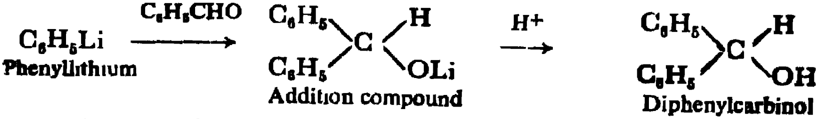


$$R—\overset{\overset{O}{\|}}{C}—OLi \xrightarrow{RLi} R—\underset{\underset{OLi}{|}}{\overset{\overset{R}{|}}{C}}—OLi \xrightarrow[\text{Hydrolysis}]{H^+} \underset{\text{Ketone}}{R—\overset{\overset{R}{|}}{C}=O}$$

Carboxylic acids may also be used directly to prepare ketones.



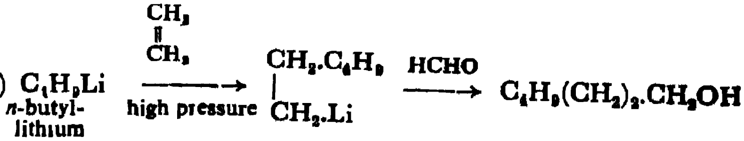
(4) With aldehydes secondary alcohols are formed (formaldehyde gives primary alcohols) while ketones give tertiary alcohols.



Yields are better than in case of Grignard reagents.

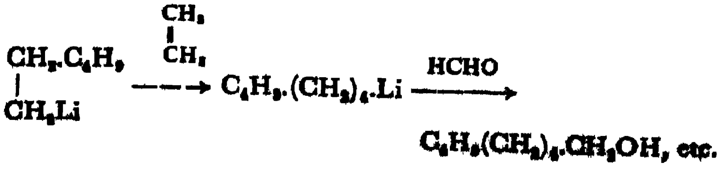
(5) Unlike Grignard reagents, alkyllithiums can add to an olefinic double bond (C=C). This reaction can be used for *stepping up* the chain, *e.g.*,

(a)



$$\underset{\substack{n\text{-butyl-}\\ \text{lithium}}}{C_4H_9Li} \xrightarrow[\text{high pressure}]{\overset{CH_2}{\underset{CH_2}{\|}}} \underset{\underset{CH_2.Li}{|}}{CH_2.C_4H_9} \xrightarrow{HCHO} C_4H_9(CH_2)_2.CH_2OH$$

(b)



$$\underset{\underset{CH_2Li}{|}}{CH_2.C_4H_9} \xrightarrow{\overset{CH_2}{\underset{CH_2}{\|}}} C_4H_9.(CH_2)_4.Li \xrightarrow{HCHO} C_4H_9(CH_2)_4.CH_2OH, \text{ etc.}$$

A mixture of alcohols containing 7 to 13 carbon atoms is obtained.

ORGANOLEAD COMPOUNDS

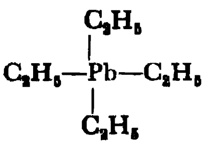
9. **Tetraethyllead, TEL.**—The only organolead compound which is important is tetraethyllead. It is of greatest industrial importance and is commonly referred to in the industry as TEL.

Preparation. This is manufactured by heating ethyl chloride with sodium-lead alloy under pressure.

$$4C_2H_5Cl+4Na/Pb \rightarrow \underset{\text{Tetraethyllead}}{(C_2H_5)_4Pb} +3Pb+4NaCl$$

Tetraethyllead in the reaction mixture is distilled off with superheated steam at 473K.

Properties. Tetraethyllead is a colourless liquid (density= 1·659 ; b.p. about 473K). It is insoluble in water but soluble in ether. It is highly poisonous and requires special precautions in handling. It is absorbed both by the lungs and through the skin. It is a purely covalent compound.



$$\begin{array}{c} C_2H_5 \\ | \\ C_2H_5—Pb—C_2H_5 \\ | \\ C_2H_5 \end{array}$$

Uses. It is used for raising the octane number of petrol (*see* page 2·85). One part of TEL per thousand parts of petrol is used. To prevent lead from being deposited in the cylinder head, small amount of ethylene bromide is added. This converts lead into lead dibromide which is sufficiently volatile and is removed with the exhaust gases.

QUESTIONS

Essay Type :

1. How is a Grignard reagent prepared ? Describe the uses of this reagent for the preparation of different types of organic compounds.
(*Jammu B.Sc. 1975* ; *Kerala 1975* ; *Delhi B.Sc. Hons. 1973*)

2. How can Grignard reagent be prepared ? What special precautions are to be taken in its preparation ? How can it be used in the synthesis of (*a*) propionic acid, (*b*) *n*-butyl alcohol, (*c*) trimethylcarbinol, and (*d*) propionaldehyde ?
(*Rajasthan B.Sc. 1971*)

3. Describe in detail the preparation of ethylmagnesium iodide in the laboratory. Give the importance of the compound in organic synthesis.
(*Delhi B.Sc. 1977* ; *Shivaji 1976*)

4. How would you prepare an ethereal solution of ethylmagnesium bromide ? Show how this solution may be used for the synthesis of (*a*) propionic acid, (*b*) *n*-butyl alcohol, (*c*) dimethylcarbinol, (*d*) propionaldehyde.
(*Delhi B.Sc. Supp. 1976*)

5. (*a*) What are organometallic compounds ? How is pure sample of ethylmagnesium bromide prepared ?

(*b*) How can ethylmagnesium bromide be used in the synthesis of (*i*) 1-Butanol, (*ii*) 2-Butanol, (*iii*) 2-Methyl-2-butanol, (*iv*) Propionic acid. (*v*) Propionaldehyde (*vi*) Methoxypropane ?
(*Delhi B.Sc. Hons. 1981*, *Delhi B.Sc. 1978 Supp.*)

Short Answer Type :

1. Starting from a suitable Grignard reagent outline the synthesis of

2. Write a short note on the structure of Grignard reagent.

3. Discuss the mechanism of the reaction of ethylene oxide with Grignard reagent.

4. Write equations for the reactions, if any, between :

(1) Magnesium+Ethyl iodide in dry ether.

(2) Grignard reagent + water ; alcohol ; ethylamine ; alkyl iodide : allyl bromide ; propyne ; α-monochloroether ; ethyl formate : acyl chloride : chloroformic ester ; cyanogen chloride ; chloramine ; iodine ; mercuric chloride ; lead chloride.

(3) Addition of the following compounds to Grignard reagent followed by hydrolysis ; formaldehyde ; ethylene oxide ; acetaldehyde ; acetone ; ethyl orthoformate ; alkyl cyanide ; carbon dioxide ; sulphur ; carbon disulphide.

(4) Zinc + alkyl iodide.

(5) Dimethylzinc+acetaldehyde ; acetone ; water ; ethyl iodide ; acetyl chloride ; *tert.* butyl iodide.

(6) Li+RX ; *n*-C_4H_9 Cl ; R'X

(7) RLi+H_2O ; $AuBr_3$; CO_2 ; RCOOH

(8) $C_6H_{11}Li+CH_2=CH_2$ and then HCHO

(9) $C_6H_5Li+C_6H_5CHO$ and then H^+.

(10) Ethyl chloride+sodium-lead alloy.

5. Write a note on the preparation and synthetic uses of organometallic compounds of zinc.

6. Describe the preparation, principal properties and uses of tetraethyl-lead (TEL).

7. "Grignard reagents have attained a position in organic chemistry unrivalled by any other class of compounds." Justify this statement.

(*Guru Nanak Dev B. Sc. 1971*)

Problems :

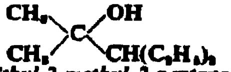
1. An organic compound $C_3H_6Cl_2$ (A) gives with alkali C_3H_6O (B) or C_3H_4 (C). The compound **B** gives with ethylmagnesium iodide $C_5H_{12}O$ (D) which forms an iodide (E). Compound **C** reacts with dilute sulphuric acid containing mercuric sulphate to give C_3H_6O (F) which gives with bromine in alkali the salt of $C_2H_4O_2$ (G). The Grignard reagent from **E** reacts with **F** to give $C_8H_{18}O$ (H). Identify the compounds **A** to **H**.

2. The organic compound C_3H_6 (A) reacts with chlorine to give either $C_3H_6Cl_2$ (B) or C_3H_5Cl (C) depending upon the temperature. With ethylmagnesium iodide C gives C_5H_{10} (D). Identify the compounds A to D.

3. With aqueous potash C_3H_7I (A) gives C_3H_8O (B) which may be oxidised only to C_3H_6O (C). The Grignard reagent from **A** reacts with **C** to give $C_6H_{14}O$ (D). Identify the compounds A to D.

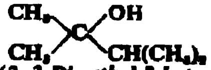
4. On careful reduction C_2H_2 (A) gives C_2H_4 (B) which reacts with hydriodic acid to give C_2H_5I (C). A forms a di-Grignard derivative which reacts with C to give mainly C_6H_{10} (D). With dilute sulphuric acid containing mercuric sulphate D gives $C_6H_{12}O$ (E) which reacts with the Grignard derivative of C to give $C_8H_{18}O$ (F). On oxidation D gives $C_2H_4O_2$ (G) which gives acid chloride H. This reacts with one molecule of the Grignard reagent from **C** to give $C_4H_{10}O$ (I). With two molecules of the same Grignard reagent H gives $C_7H_{16}O$ (J). Identify the compounds A to J

ANSWERS

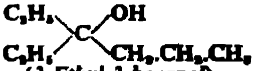
1. **A** is $CH_3.CH_2.CHCl_2$; **B** is C_2H_5CHO (*Propionaldehyde*)
(*Propylidene chloride*)
C is $CH_3.C{\equiv}CH$ (*Propyne*) ; **D** is $(C_2H_5)_2CHOH$ (*3-Pentanol*) ;
E is $(C_2H_5)_2CHI$ (*3-Iodopentane*) ; **F** is CH_3COCH_3 (*Acetone*) ;
G is CH_3COOH (*Acetic acid*) ;
H is


(*3-Ethyl-2-methyl-2-pentanol*)

2. **A** is $CH_3.CH{=}CH_2$ (*Propene*)
B is $CH_3.CHCl.CH_2Cl$ (*Propylene chloride*)
C is $CH_2{=}CH{-}CH_2Cl$ (*Allyl chloride*)
D is $CH_2{=}CH.CH_2.C_2H_5$ (*1-Pentene*)

3 **A** is $CH_3CHI.CH_3$ (*2-Iodopropane*) ;
B is $CH_3CHOH.CH_3$ (*2-Propanol*) ;
C is $CH_3\,CO.CH_3$ (*Acetone*) ;
D is


(*2, 3-Dimethyl-2-butanol*)

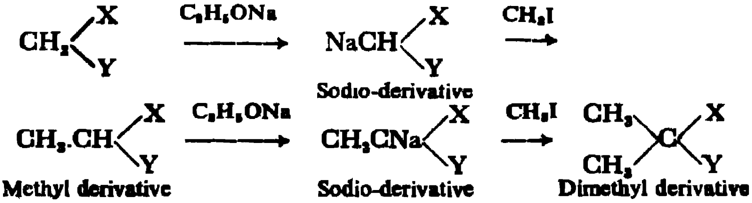
4. **A** is $CH{\equiv}CH$ (*Acetylene*) ; **B** is $CH_2{=}CH_2$ (*Ethylene*)
C is $CH_3.CH_2I$ (*Ethyl iodide*)
Di-Grignard derivative is $IMg\,C{\equiv}CMgI$
D is $C_2H_5{-}C{\equiv}C{-}C_2H_5$ (*3-Hexyne*)
E is $C_2H_5{-}CO{-}CH_2.CH_2.CH_3$ (*Ethyl n-propyl ketone*)
F is


(*3-Ethyl-3-hexanol*)
G is $C_2H_5\,COOH$ (*Propionic acid*)
H is C_2H_5COCl (*Propionyl chloride*)
I is $(C_2H_5)_2C{=}O$ (*3-Pentanone*)
J is $(C_2H_5)_3COH$ (*Triethylcarbinol or 3-Ethyl -3-pentanol*).

30

Acetoacetic, Malonic and Cyanoacetic Esters

1. **Reactive Methylene Group.**—A methylene group ($-CH_2-$) when situated between two electron-withdrawing groups (*e.g.*, $-CN$, $-COOC_2H_5$) is highly reactive and is termed reactive methylene group. The two hydrogen atoms of this can be successively replaced by sodium when treated with sodium ethoxide. For example,



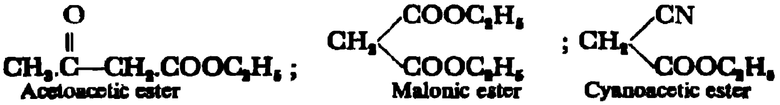
$$CH_2{<}^{X}_{Y} \xrightarrow{C_2H_5ONa} NaCH{<}^{X}_{Y} \xrightarrow{CH_3I}$$

Sodio-derivative

$$CH_3.CH{<}^{X}_{Y} \xrightarrow{C_2H_5ONa} CH_3CNa{<}^{X}_{Y} \xrightarrow{CH_3I} {}^{CH_3}_{CH_3}{>}C{<}^{X}_{Y}$$

Methyl derivative Sodio-derivative Dimethyl derivative

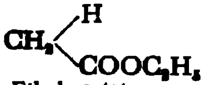
where X and Y are two electron-withdrawing groups. These reactions render various compounds containing reactive methylene groups extremely important synthetic reagents. Some such compounds containing a reactive methylene group are :



$$CH_3.\overset{O}{\overset{\|}{C}}-CH_2.COOC_2H_5 \,; \quad CH_2{<}^{COOC_2H_5}_{COOC_2H_5} \,; \quad CH_2{<}^{CN}_{COOC_2H_5}$$

Acetoacetic ester Malonic ester Cyanoacetic ester

The methylene group in ethyl acetate is situated between electropositive hydrogen atom and the negative $-COOC_2H_5$ group.



$$CH_2{<}^{H}_{COOC_2H_5}$$

Ethyl acetate

Not situated between two negative groups as it is, the methylene group in ethyl acetate is not reactive and does not give any sodio-derivative.

ACETOACETIC ESTER

2. **Acetoacetic Ester or Ethyl Acetoacetate.**—It is the ethyl ester of acetoacetic acid, $CH_3.CO.CH_2.COOH$, a β-ketonic acid. The name aceto acetic ester is given since it could be regarded as acetyl derivative of acetic ester (ethyl acetate). It is an extremely valuable synthetic reagent.

Preparation. Acetoacetic ester is prepared by the action of sodium on ethyl acetate in the presence of ethyl alcohol.

Acetoacetic ester is produced as a result of condensation between two molecules of ethyl acetate in the presence of sodium ethoxide.

$$CH_3CO|\overline{OC_2H_5 + H}|CH_2COOC_2H_5 \rightarrow \underset{\text{Acetoacetic ester}}{CH_3CO.CH_2COOC_2H_5} + C_2H_5OH$$

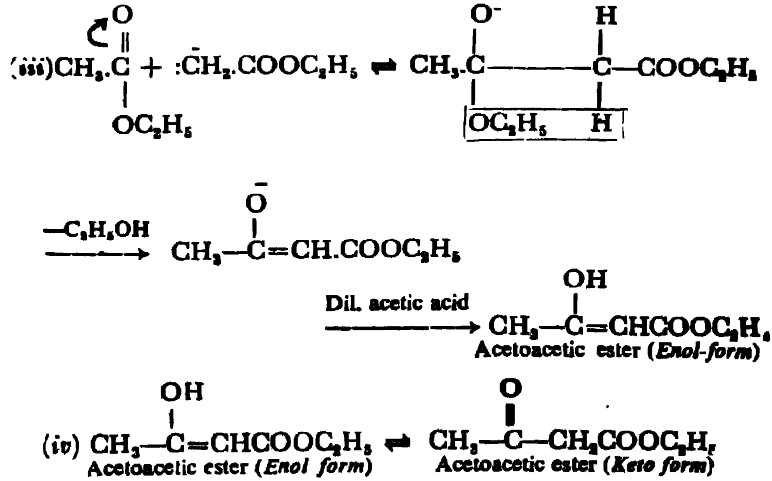
Pure ethyl acetate (10 parts) with a little alcohol is taken in a flask and to this is added clean sodium wire (1 part). A slow reaction sets in and becomes gradually vigorous with the evolution of hydrogen and boiling of the liquid. The flask is heated on a water bath after the reaction subsides till whole of sodium disappears.

The product is sodium derivative of acetoacetic ester which forms a brown semi-solid mass with sodium ethoxide and unused ethyl acetate. This is treated with dilute acetic acid (1 : 1) until acidic. This decomposes the sodium derivative and acetoacetic ester separates out as an oily layer at the top. The oily product is distilled and fraction passing between 448-453K consists of almost pure ester and is further purified by distilling under reduced pressure.

The above condensation between two molecules of ethyl acetate is termed *Claisen condensation*. It is rather a complex reaction and many mechanisms have been proposed for it. The one most widely accepted at the moment is as follows :

(*i*) $\underset{\text{Ethanol}}{C_2H_5OH} \xrightarrow{Na} \underset{\text{Sod. ethoxide}}{C_2H_5ONa} \rightleftharpoons [OC_2H_5]^- + Na^+$

(*ii*) $CH_3.COOC_2H_5 + [OC_2H_5]^- \rightleftharpoons :\bar{C}H_2.COOC_2H_5 + C_2H_5OH$



$$(iii)\ CH_3.\underset{OC_2H_5}{\overset{O}{\overset{\|}{C}}} + :\bar{C}H_2.COOC_2H_5 \rightleftharpoons CH_3.\underset{\boxed{OC_2H_5}}{\overset{O^-}{C}}\text{———}\underset{\boxed{H}}{\overset{H}{C}}\text{—}COOC_2H_5$$

$$\xrightarrow{-C_2H_5OH} CH_3\text{—}\overset{\bar{O}}{C}=CH.COOC_2H_5$$

$$\xrightarrow{\text{Dil. acetic acid}} \underset{\text{Acetoacetic ester (\textit{Enol-form})}}{CH_3\text{—}\overset{OH}{C}=CHCOOC_2H_5}$$

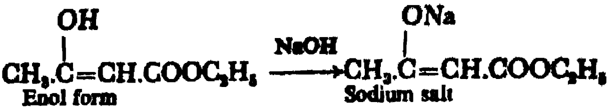
$$(iv)\ \underset{\text{Acetoacetic ester (\textit{Enol form})}}{CH_3\text{—}\overset{OH}{C}=CHCOOC_2H_5} \rightleftharpoons \underset{\text{Acetoacetic ester (\textit{Keto form})}}{CH_3\text{—}\overset{O}{\overset{\|}{C}}\text{—}CH_2COOC_2H_5}$$

Properties : **Physical**. Acetoacetic ester is a colourless liquid (b.p. 454K) having a pleasant odour. It is sparingly soluble in water but readily dissolves in alcohol, ether and most other organic solvents.

Chemical. (1) **Properties of Ketonic Group.** Acetoacetic ester behaves as a typical keto compound and gives addition compounds with HCN and $NaHSO_3$. Similarly, it gives condensation products with hydroxylamine and phenylhydrazine. It is readily reduced by sodium amalgam or catalytically to β-hydroxybutyric ester.

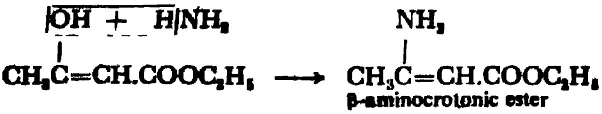
$$\underset{\text{Acetoacetic ester}}{CH_3.CO.CH_2COOC_2H_5} + 2[H] \longrightarrow \underset{\beta\text{-Hydroxybutyric ester}}{CH_3.CHOH.CH_2COOC_2H_5}$$

(2) **With dilute Alkali.** It is neutral to litmus but dissolves in dilute sodium hydroxide solution with which it reacts in its enol form.



$$\underset{\text{Enol form}}{CH_3.\overset{\overset{OH}{|}}{C}=CH.COOC_2H_5} \xrightarrow{NaOH} \underset{\text{Sodium salt}}{CH_3.\overset{\overset{ONa}{|}}{C}=CH.COOC_2H_5}$$

(3) **With Ammonia.** Acetoacetic ester reacts with ammonia to give β-aminocrotonic ester.

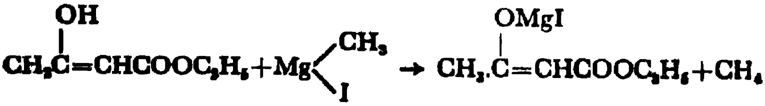


$$CH_3\overset{\overset{OH\ +\ H|NH_2}{|}}{C}=CH.COOC_2H_5 \longrightarrow \underset{\beta\text{-aminocrotonic ester}}{CH_3\overset{\overset{NH_2}{|}}{C}=CH.COOC_2H_5}$$

(4) **With Bromine.** It gives an addition product with bromine which is added at the double bond.

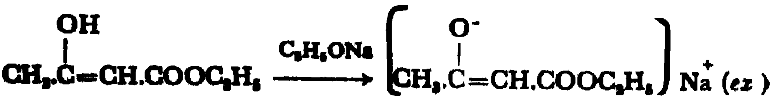
(5) **With Ferric chloride.** It gives a violet red colour with ferric chloride—a property of $—\overset{\overset{OH}{|}}{C}=C—$ group (*see* Phenol).

(6) **With Grignard reagent.** Acetoacetic ester reacts with Grignard reagent to form a hydrocarbon. This also shows that Grignard reagent reacts with the enol form.



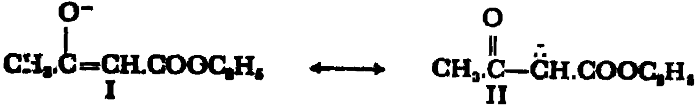
$$CH_3\overset{\overset{OH}{|}}{C}=CHCOOC_2H_5 + Mg\begin{smallmatrix}\nearrow CH_3\\ \searrow I\end{smallmatrix} \rightarrow CH_3.\overset{\overset{OMgI}{|}}{C}=CHCOOC_2H_5 + CH_4$$

(7) **Formation of Sodio and Alkyl Derivatives.** It reacts with sodium ethoxide to give sodio-derivative.



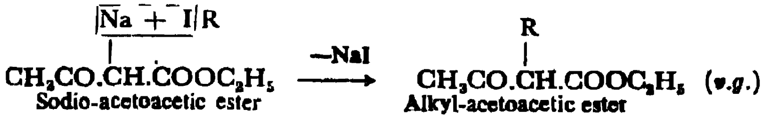
$$CH_3.\overset{\overset{OH}{|}}{C}=CH.COOC_2H_5 \xrightarrow{C_2H_5ONa} \left[CH_3.\overset{\overset{O^-}{|}}{C}=CH.COOC_2H_5\right]\overset{+}{Na}\ (ex\ )$$

The negative ion is a resonance hybrid of two structures :



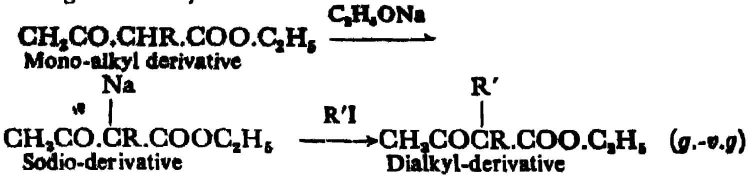
$$\underset{I}{CH_3.\overset{\overset{O^-}{|}}{C}=CH.COOC_2H_5} \longleftrightarrow \underset{II}{CH_3.\overset{\overset{O}{\|}}{C}—\overset{\cdot\cdot\,-}{C}H.COOC_2H_5}$$

i.e., this ion is ambident. It reacts with primary and secondary alkyl halides to give alkyl derivative of acetoacetic ester in which the alkyl group is attached to carbon atom. This is because negatively charged carbon atom is more reactive than negatively charged oxygen atom.



$$\overset{\overline{|Na^{-}+^{-}I|R}}{\underset{\text{Sodio-acetoacetic ester}}{CH_3CO.\dot{C}H.COOC_2H_5}} \xrightarrow{-NaI} \overset{R}{\underset{\text{Alkyl-acetoacetic ester}}{CH_3CO.CH.COOC_2H_5}} \;(v.g.)$$

The whole process may be repeated with the mono-alkyl derivative to get a dialkyl derivative.

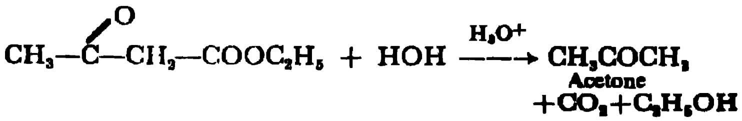


$$\underset{\text{Mono-alkyl derivative}}{CH_3CO.CHR.COO.C_2H_5} \xrightarrow{C_2H_5ONa}$$

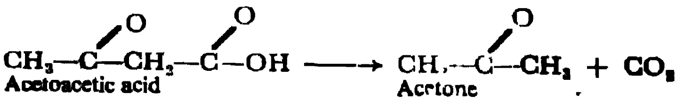
$$\underset{\text{Sodio-derivative}}{CH_3CO.\overset{Na}{C}R.COOC_2H_5} \xrightarrow{R'I} \underset{\text{Dialkyl-derivative}}{CH_3CO\overset{R'}{C}R.COO.C_2H_5} \;(g.-v.g)$$

It is important to note that two alkyl groups can only be introduced in two steps as given above.

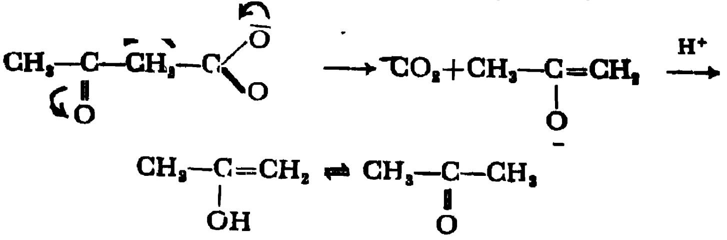
(8) **Ketonic Hydrolysis.** This is so called because a ketone is the chief product of hydrolysis and is carried out by boiling with dilute acid or dilute alkali, preferably acid solution.



The first step in the reaction is a simple hydrolysis of the ester group to give the acetoacetic acid, but when two COOH groups or a C=O and a COOH group are attached to the same carbon atom, the compound readily loses carbon dioxide. Thus the acetoacetic acid loses CO_2 during the hydrolysis to yield the ketone.



The mechanism of ketonic hydrolysis is probably as under:

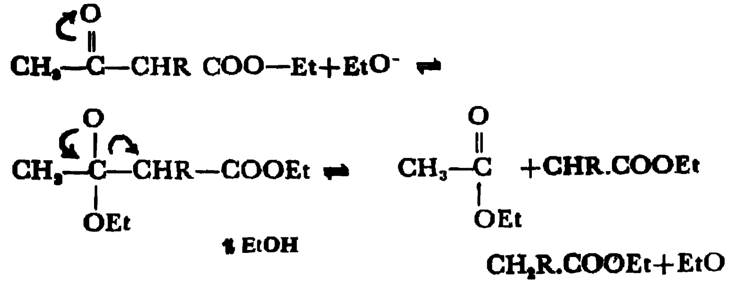


It is the electron-attracting property of the carbonyl group which facilitates the elimination of one CO_2 molecule.

(9) **Acid Hydrolysis.** This is so called because an acid is the chief product of hydrolysis and is carried out by boiling with concentrated alcoholic potash.

$$CH_3\overset{OH}{CO}|\overset{H}{CH_2}\overset{OH}{CO}|\overset{H}{OC_2H_5} \xrightarrow{2KOH} 2CH_3COOK+C_2H_5OH$$

The possible mechanism of the reaction is

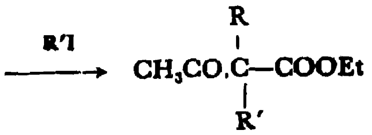


3. Use of Acetoacetic Ester in Organic Synthesis.—Acetoacetic ester is an important synthetic reagent. Its synthetic importance lies in the large number of substances which can be synthesised from it. Following are some of its important examples :

(1) **Synthesis of alkyl acetoacetic ester.** Acetoacetic ester is treated with sodium ethoxide and the sodio-derivative so obtained is further treated with alkyl iodide when we get monoalkyl acetoacetic ester. The monoalkyl derivative may again be treated with C_2H_5ONa and then with alkyl iodide to get dialkyl derivative.

$$\underset{\text{Acetoacetic ester}}{CH_3CO.CH_2COOEt} \xrightarrow{C_2H_5ONa} \underset{\text{Sodio-acetoacetic ester}}{CH_3COCHNaCOOEt} \xrightarrow{RI}$$

$$\underset{\text{Monoalkylacetoacetic ester}}{CH_3COCHR.COOEt} \xrightarrow{C_2H_5ONa} \underset{\text{Sodio-derivative of monoalkylacetoacetic ester}}{CH_3.CO.CRNa.COOEt}$$



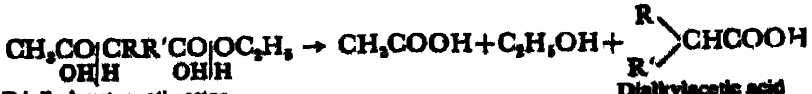
$$\xrightarrow{R'I} CH_3CO.\overset{R}{\underset{R'}{C}}-COOEt$$

Dialkylacetoacetic ester

(2) **Synthesis of fatty acids.** When acetoacetic ester or its alkyl derivatives are *heated with concentrated alcoholic potash* (**acid hydrolysis**), fatty acids are produced.

$$CH_3\overset{OH}{CO}|\overset{H}{CH_2}\overset{OH}{CO}|\overset{H}{OC_2H_5} \xrightarrow{OH^-} 2CH_3COOH+C_2H_5OH$$

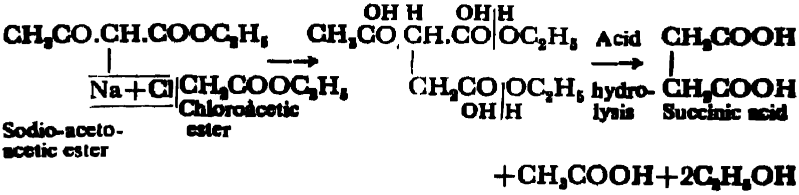
$$\underset{\text{Monoalkylacetoacetic ester}}{CH_3\underset{OH}{CO}|\underset{H}{CHR}.\underset{OH}{CO}|\underset{H}{OC_2H_5}} \xrightarrow{\text{conc.}} CH_3COOH+\underset{\text{Monoalkylacetic acid}}{RCH_2COOH}+C_2H_5OH$$



$$\underset{\text{Dialkylacetoacetic ester}}{CH_3\underset{OH}{CO}|\underset{H}{CRR'}\underset{OH}{CO}|\underset{H}{OC_2H_5}} \rightarrow CH_3COOH+C_2H_5OH+\underset{\text{Dialkylacetic acid}}{\overset{R}{\underset{R'}{>}}CHCOOH}$$

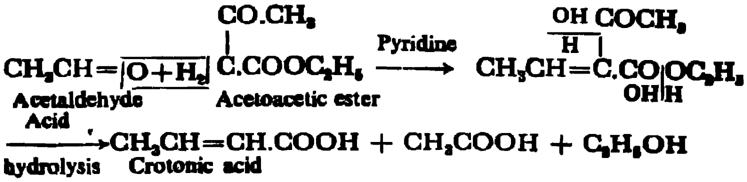
Since acetic acid is water soluble and the substituted acetic acid probably will not be, the two are easily separated. Otherwise they would be separated by fractional distillation.

(3) **Synthesis of dibasic acids.** When sodio-derivative of acetoacetic ester is condensed with a chloro fatty acid and the product subjected to acid hydrolysis a dibasic acid is obtained.



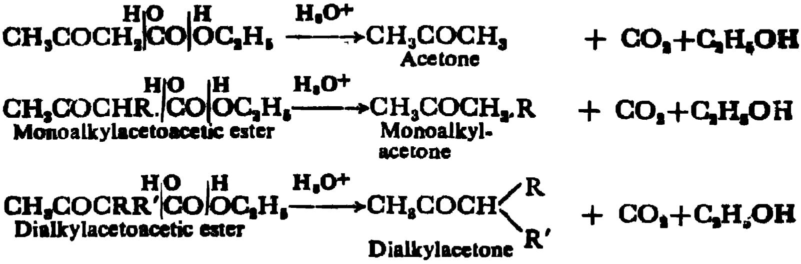
$$\underset{\text{Sodio-aceto-acetic ester}}{CH_3CO.\overset{}{CH}(Na).COOC_2H_5} + \underset{\text{Chloroacetic ester}}{Cl\,CH_2COOC_2H_5} \longrightarrow CH_3CO.\underset{\underset{CH_2CO|OC_2H_5}{|}}{CH}.CO|OC_2H_5 \xrightarrow[\text{hydrolysis}]{\text{Acid}} \underset{\text{Succinic acid}}{\underset{CH_2COOH}{\overset{CH_2COOH}{|}}} + CH_3COOH + 2C_2H_5OH$$

(4) **Synthesis of α, β-unsaturated acids.** Acetoacetic ester undergoes the *Knoevenagel reaction* due to the presence of an active methylene group. It condenses with aldehydes or ketones in presence of a base and the products on acid hydrolysis yield α, β-unsaturated acids.



$$\underset{\text{Acetaldehyde}}{CH_3CH{=}O} + \underset{\text{Acetoacetic ester}}{H_2C(CO.CH_3).COOC_2H_5} \xrightarrow{\text{Pyridine}} CH_3CH{=}\overset{COCH_3}{C}.CO|OC_2H_5 \xrightarrow[\text{hydrolysis}]{\text{Acid}} \underset{\text{Crotonic acid}}{CH_3CH{=}CH.COOH} + CH_3COOH + C_2H_5OH$$

(5) **Synthesis of ketones.** When acetoacetic ester or its alkyl derivatives are *heated with dilute acid or alkali, preferably acid* (**ketonic hydrolysis**), ketones are obtained.

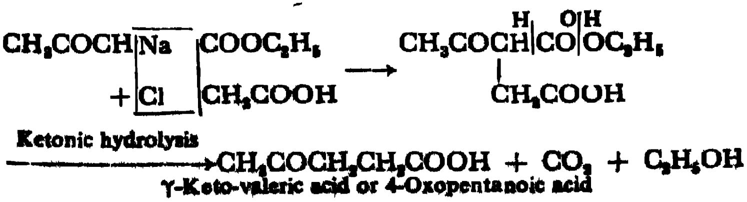


$$CH_3COCH_2|CO|OC_2H_5 \xrightarrow{H_3O^+} \underset{\text{Acetone}}{CH_3COCH_3} + CO_2 + C_2H_5OH$$

$$\underset{\text{Monoalkylacetoacetic ester}}{CH_3COCHR.|CO|OC_2H_5} \xrightarrow{H_3O^+} \underset{\text{Monoalkylacetone}}{CH_3COCH_2.R} + CO_2 + C_2H_5OH$$

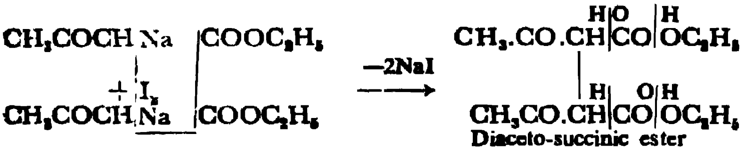
$$\underset{\text{Dialkylacetoacetic ester}}{CH_3COCRR'|CO|OC_2H_5} \xrightarrow{H_3O^+} \underset{\text{Dialkylacetone}}{CH_3COCH\langle^{R}_{R'}} + CO_2 + C_2H_5OH$$

(6) **Synthesis of γ-ketonic acids.** When sodio-derivative of acetoacetic ester is treated with α-chloro fatty acids and the product is submitted to *ketonic hydrolysis*, we get γ-ketonic acids.



$$CH_3COCH(Na)COOC_2H_5 + Cl\,CH_2COOH \longrightarrow CH_3COCH(CH_2COOH)|CO|OC_2H_5 \xrightarrow{\text{Ketonic hydrolysis}} \underset{\gamma\text{-Keto-valeric acid or 4-Oxopentanoic acid}}{CH_3COCH_2CH_2COOH} + CO_2 + C_2H_5OH$$

(7) **Synthesis of diacetosuccinic ester and acetonylacetone.** Two molecules of sodioacetoacetic ester condense when treated with iodine and diacetosuccinic ester is produced. The product on ketonic hydrolysis gives acetonylacetone.



$$\begin{array}{l} CH_3COCH\,Na \\ \quad | \quad + I_2 \\ CH_3COCH\,Na \end{array} \begin{array}{l} COOC_2H_5 \\ \\ COOC_2H_5 \end{array} \xrightarrow{-2NaI} \begin{array}{l} CH_3.CO.CH\,CO\,OC_2H_5 \\ \quad\;\; | \\ CH_3CO.CH\,CO\,OC_2H_5 \end{array}$$

Diaceto-succinic ester

$$\xrightarrow{\text{Ketonic hydrolysis}} CH_3COCH_2.CH_2CO.CH_3+2CO_2+2C_2H_5OH$$

Acetonylacetone
or 2,5-pentadione

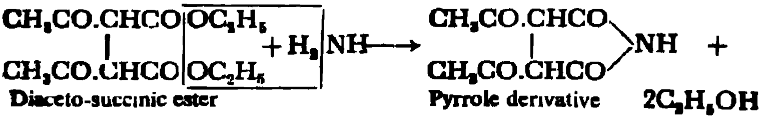
(8) **Synthesis of hydrocarbons.** On electrolytic reduction, acetoacetic ester and its alkyl derivatives give rise to hydrocarbons.

$CH_3.COCH_2COOC_2H_5 \longrightarrow CH_3CH_2CH_2CH_3$
Acetoacetic ester — *n*-butane

$CH_3COCHRCOOC_2H_5 \longrightarrow CH_3.CH_2CHRCH_3$
Alkylacetoacetic ester — 2-alkylbutane

(9) **Synthesis of heterocyclic compounds.** Acetoacetic ester condenses with various reagents to form different types of cyclic compounds. The following may be given as typical examples :

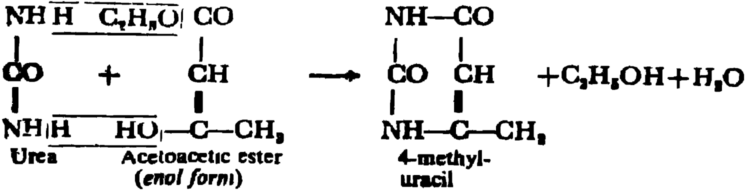
(*i*) Diacetosuccinic ester obtained in (7) above by condensing two molecules of sodio-acetoacetic ester in presence of iodine, when treated with ammonia gives pyrrole derivative.



$$\begin{array}{l} CH_3CO.CHCO\,OC_2H_5 \\ \qquad\quad | \\ CH_3CO.CHCO\,OC_2H_5 \end{array} + H_2NH \longrightarrow \begin{array}{l} CH_3CO.CHCO \\ \qquad\quad | \\ CH_3CO.CHCO \end{array}\!\!>NH + 2C_2H_5OH$$

Diaceto-succinic ester — Pyrrole derivative

(*ii*) With urea it gives the ring compound, 4-methyl-uracil from which uric acid may be synthesised.



$$\begin{array}{l} NH\,H \\ | \\ CO \\ | \\ NH\,H \end{array} + \begin{array}{l} C_2H_5O\;CO \\ \qquad\quad | \\ \qquad\; CH \\ \qquad\quad \| \\ HO—C—CH_3 \end{array} \longrightarrow \begin{array}{l} NH—CO \\ |\qquad | \\ CO\quad CH \\ |\qquad \| \\ NH—C—CH_3 \end{array} + C_2H_5OH + H_2O$$

Urea — Acetoacetic ester (*enol form*) — 4-methyl-uracil

4. Constitution of Acetoacetic Ester.

(*a*) From analytical data the **molecular formula** of acetoacetic ester is found to be $C_6H_{10}O_3$.

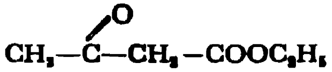
(*b*) **It behaves as a typical keto-compound** as will be clear rom the following :

(*i*) It gives characteristic compounds with HCN, $NaHSO_3$, NH_2OH and $NH_2.NH.C_6H_5$ (*reactions of* $>C=O$ *group*).

(*ii*) On reduction, the ester yields β-hydroxybutyric ester, $CH_3CH(OH).CH_2COOC_2H_5$, having a secondary alcoholic group, which must have been obtained by reduction of ketonic group.

(*iii*) On ketonic hydrolysis with dilute acid or alkalis or superheated steam at 473K, it yields acetone, alcohol and CO_2.

These reactions support the presence of a keto group in the molecule of the ester which should, therefore, be represented by the formula :



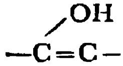
$$CH_3-\overset{O}{C}-CH_2-COOC_2H_5$$

(*c*) **Some other reactions as given below indicate, on the other hand, presence of an —OH group and a double bond in the molecule.**

(*i*) Metallic sodium liberates hydrogen and forms sodio-derivative (*a characteristic property of —OH group as in C_2H_5OH*).

(*ii*) The ester is neutral to litmus but is soluble in alkalis. This shows the presence of an —OH group acidic in nature.

(*iii*) It gives a violet red coloration with ferric chloride in alcoholic solution, a property characteristic of compounds containing



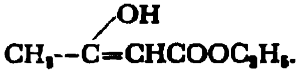
a $-\overset{OH}{C}=C-$ group as in phenols.

(*iv*) The ester gives an addition product with bromine, a property characteristic of compounds containing a double bond.

(*v*) With ammonia, acetoacetic ester gives β-amino-crotonic

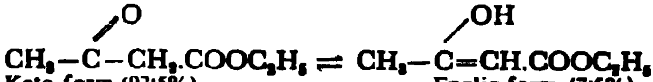
ester—($CH_3\overset{NH_2}{C}=CHCOOC_2H_5$), an unsaturated compound.

Therefore, the formula of the ester containing a double bond and an —OH group should be represented as



$$CH_3-\overset{OH}{C}=CHCOOC_2H_5.$$

(*d*) **This dual behaviour,** *as that of a keto compound and an unsaturated hydroxy compound, shown by acetoacetic ester can best be explained by assuming the ordinary ester to be a tautomeric mixture of both ketonic and enolic varieties.*



$$\underset{\text{Keto form (92·5\%)}}{CH_3-\overset{O}{C}-CH_2.COOC_2H_5} \rightleftharpoons \underset{\text{Enolic form (7·5\%)}}{CH_3-\overset{OH}{C}=CH.COOC_2H_5}$$

Keto form (92·5%) Enolic form (7·5%)

If any of these varieties be removed, more of it will be formed to maintain equilibrium. For example, when keto variety is removed by reaction with HCN, equilibrium shifts to the left and more and more of 7·5% enolic form is transformed into the keto form.

(*e*) **This explanation is further proved to be correct by the following facts :**

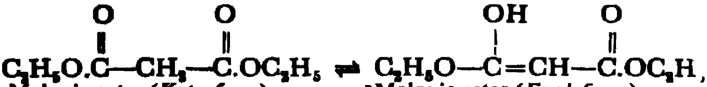
(*i*) Knorr (1911) succeeded in actual separation of the two varieties. The keto form was obtained by crystallizing the ordinary mixture from light petroleum at 195K. The enolic form was separated as colourless oil by distilling the mixture under high vacuum. He studied their properties and found that the keto variety (colourless crystals of m.p. 234K) gives no colour with ferric chloride and readily takes up bromine.

(*ii*) With rise of temperature, each form isomerises into an equilibrium mixture of keto and enol varieties.

(*iii*) That the ester is an equilibrium mixture of the two varieties is also shown by molecular refraction and other physical properties.

MALONIC ESTER

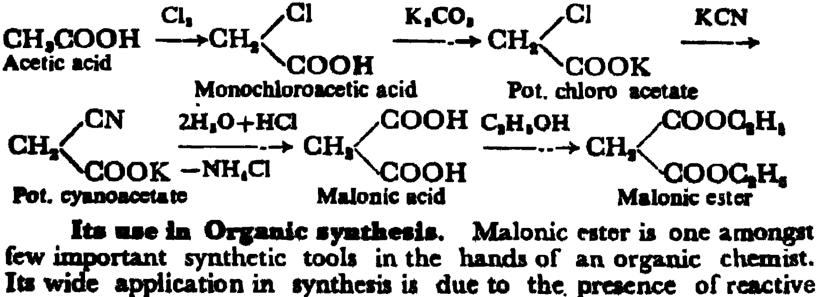
5. Diethyl Malonate or Malonic Ester, $CH_2(COOC_2H_5)_2$.—Malonic ester is the diethyl ester of malonic acid. It is a colourless liquid (b.p. 472K) with a pleasant odour. Like acetoacetic ester it contains one reactive methylene group and exists as a tautomeric mixture of *keto* and *enol* forms.



$$\underset{\text{Malonic ester (Keto form)}}{C_2H_5O.\overset{\overset{\large O}{\|}}{C}-CH_2-\overset{\overset{\large O}{\|}}{C}.OC_2H_5} \rightleftharpoons \underset{\text{*Malonic ester (Enol form)}}{C_2H_5O-\overset{\overset{\large OH}{|}}{C}=CH-\overset{\overset{\large O}{\|}}{C}.OC_2H_5}$$

Preparation. It is obtained from acetic acid which is chlorinated to monochloroacetic acid. The monochloroacetic acid is further neutralized in aqueous solution with K_2CO_3 and the resulting potassium salt solution is heated with KCN till the vigorous reaction set in has subsided. The solution of the potassium cyanoacetate so obtained is evaporated to dryness on a sand bath with constant stirring.

The residue is powdered and heated with an equal amount of absolute alcohol in a flask through which dry hydrogen chloride gas is then passed to saturate the mixture. The product is cooled and poured in ice-cold water. The malonic ester so obtained is extracted with ether. The ethereal solution is washed, dried and distilled to recover ether. The oily residue is further purified by fractional distillation and fraction passing between 468-478K collected, which is pure malonic ester.

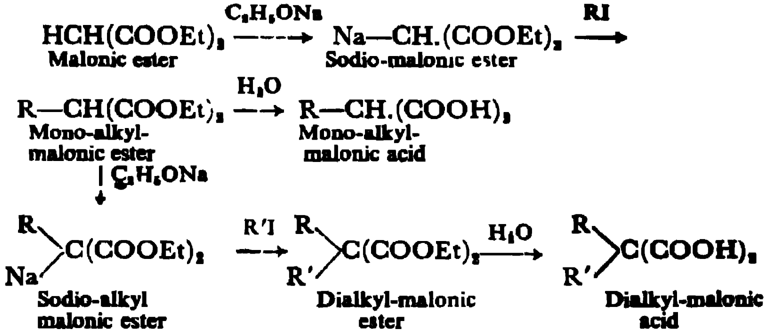


Its use in Organic synthesis. Malonic ester is one amongst few important synthetic tools in the hands of an organic chemist. Its wide application in synthesis is due to the presence of reactive methylene group. The hydrogen atoms in this methylene group are reactive due to their position between two negative groups (having tendency to attract electrons). One of these is readily replaced by sodium when treated with alcoholic solution of sodium ethoxide. The following examples will show its importance in organic synthesis :

(1) **Synthesis of substituted malonic acids.** Malonic ester gives its sodio-derivative when boiled with alcoholic solution of sodium ethoxide or metallic sodium in alcohol. The sodio-derivative forms with alkyl iodide mono-substituted ester. The second hydrogen atom may similarly be replaced to obtain substituted ester.

It is the enolic form of the acid that gives sodio-derivative which is a resonance hybrid of two varieties. On reacting the sodio-derivative with alkyl halide, etc., the alkyl group attaches with the carbon atom. In the following discussion, however, simple formulae have been used for the sake of convenience.

The esters on hydrolysis will produce the corresponding acids.



$$\underset{\text{Malonic ester}}{HCH(COOEt)_2} \xrightarrow{C_2H_5ONa} \underset{\text{Sodio-malonic ester}}{Na—CH.(COOEt)_2} \xrightarrow{RI}$$

$$\underset{\text{Mono-alkyl-malonic ester}}{R—CH(COOEt)_2} \xrightarrow{H_2O} \underset{\text{Mono-alkyl-malonic acid}}{R—CH.(COOH)_2}$$

$$\downarrow C_2H_5ONa$$

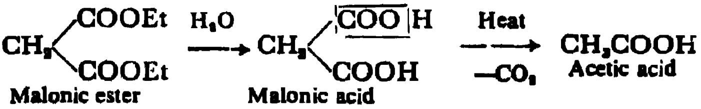
$$\underset{\text{Sodio-alkyl malonic ester}}{\begin{matrix} R \\ Na \end{matrix}\!\!>C(COOEt)_2} \xrightarrow{R'I} \underset{\text{Dialkyl-malonic ester}}{\begin{matrix} R \\ R' \end{matrix}\!\!>C(COOEt)_2} \xrightarrow{H_2O} \underset{\text{Dialkyl-malonic acid}}{\begin{matrix} R \\ R' \end{matrix}\!\!>C(COOH)_2}$$

The disubstituted derivative can be prepared *in one step* by treating the ester with two equivalents of C_2H_5ONa and then with two equivalents of alkyl halide (*cf*. Acetoacetic ester).

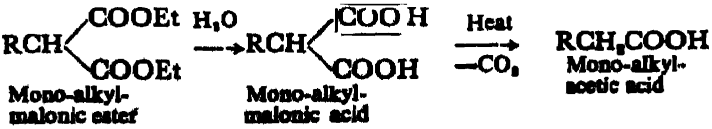
$$\underset{\text{Malonic ester}}{CH_2(COOC_2H_5)_2} \xrightarrow{2C_2H_5ONa} \underset{\text{Disodiomalonic ester}}{Na_2C(COOC_2H_5)_2} \xrightarrow{2RX} \underset{\text{Dialkyl malonic ester}}{R_2C(COOC_2H_5)_2}$$

$$\xrightarrow{H_2O} \underset{\text{Dialkyl malonic acid}}{R_2C(COOH)_2}$$

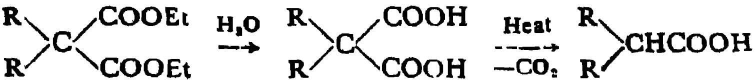
(2) **Synthesis of fatty acids.** Malonic ester or substituted malonic ester on hydrolysis and subsequent heating gives a fatty acid with loss of carbon dioxide.



$$\underset{\text{Malonic ester}}{CH_2\!<\!\begin{matrix} COOEt \\ COOEt \end{matrix}} \xrightarrow{H_2O} \underset{\text{Malonic acid}}{CH_2\!<\!\begin{matrix} \boxed{COO}H \\ COOH \end{matrix}} \xrightarrow[-CO_2]{\text{Heat}} \underset{\text{Acetic acid}}{CH_3COOH}$$



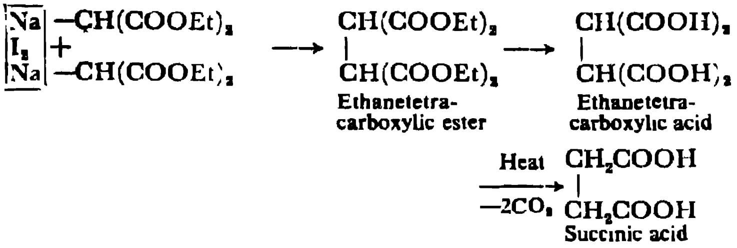
$$\underset{\text{Mono-alkyl-malonic ester}}{RCH\!<\!\begin{matrix} COOEt \\ COOEt \end{matrix}} \xrightarrow{H_2O} \underset{\text{Mono-alkyl-malonic acid}}{RCH\!<\!\begin{matrix} \boxed{COO}H \\ COOH \end{matrix}} \xrightarrow[-CO_2]{\text{Heat}} \underset{\text{Mono-alkyl-acetic acid}}{RCH_2COOH}$$



Dialkyl-malonic ester → Dialkyl-malonic acid → Dialkyl-acetic acid

(3) **Synthesis of dibasic and other polybasic acids.**

(*i*) Sodio-malonic ester with iodine yields a tetracarboxylic ester which on hydrolysis and subsequent heating yields succinic acid

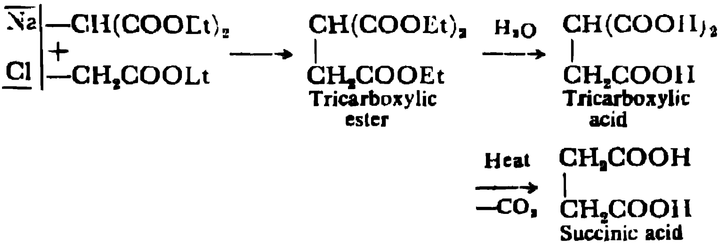


$$\begin{array}{l}\text{Na}-\text{CH(COOEt)}_2\\ \text{I}_2 \quad +\\ \text{Na}-\text{CH(COOEt)}_2\end{array} \longrightarrow \begin{array}{l}\text{CH(COOEt)}_2\\ |\\ \text{CH(COOEt)}_2\end{array} \longrightarrow \begin{array}{l}\text{CH(COOH)}_2\\ |\\ \text{CH(COOH)}_2\end{array} \xrightarrow[-2\text{CO}_2]{\text{Heat}} \begin{array}{l}\text{CH}_2\text{COOH}\\ |\\ \text{CH}_2\text{COOH}\end{array}$$

Ethanetetra-carboxylic ester; Ethanetetra-carboxylic acid; Succinic acid

Similarly starting with sodio-alkylmalonic ester, we get dialkyl-succinic acid.

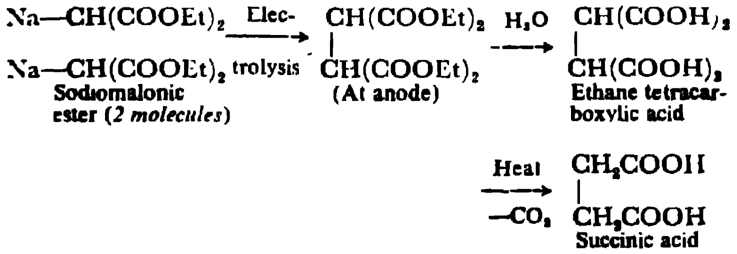
(*ii*) Sodiomalonic ester may also be treated with a halogen substituted fatty acid to get a dibasic acid.



$$\begin{array}{l}\text{Na}-\text{CH(COOEt)}_2\\ \quad +\\ \text{Cl}-\text{CH}_2\text{COOEt}\end{array} \longrightarrow \begin{array}{l}\text{CH(COOEt)}_2\\ |\\ \text{CH}_2\text{COOEt}\end{array} \xrightarrow{\text{H}_2\text{O}} \begin{array}{l}\text{CH(COOH)}_2\\ |\\ \text{CH}_2\text{COOH}\end{array} \xrightarrow[-\text{CO}_2]{\text{Heat}} \begin{array}{l}\text{CH}_2\text{COOH}\\ |\\ \text{CH}_2\text{COOH}\end{array}$$

Tricarboxylic ester; Tricarboxylic acid; Succinic acid

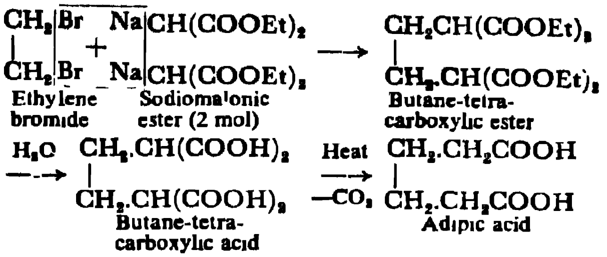
(*iii*) Sodiomalonic ester on electrolysis gives tetracarboxylic ester which on hydrolysis and subsequent heating finally yields succinic acid.



$$\begin{array}{l}\text{Na}-\text{CH(COOEt)}_2\\ \\ \text{Na}-\text{CH(COOEt)}_2\end{array} \xrightarrow[\text{trolysis}]{\text{Elec-}} \begin{array}{l}\text{CH(COOEt)}_2\\ |\\ \text{CH(COOEt)}_2\end{array} \xrightarrow{\text{H}_2\text{O}} \begin{array}{l}\text{CH(COOH)}_2\\ |\\ \text{CH(COOH)}_2\end{array} \xrightarrow[-\text{CO}_2]{\text{Heat}} \begin{array}{l}\text{CH}_2\text{COOH}\\ |\\ \text{CH}_2\text{COOH}\end{array}$$

Sodiomalonic ester (*2 molecules*); (At anode); Ethane tetracarboxylic acid; Succinic acid

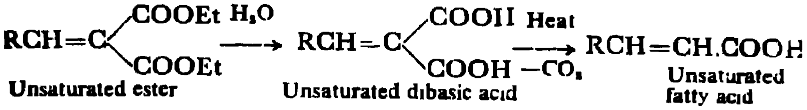
(4) **Synthesis of higher dibasic acids.** Sodiomalonic ester when treated with an alkylene halide with two halogen atoms in the end positions yields higher dibasic acids.



Ethylene bromide + Sodiomalonic ester (2 mol) → Butane-tetra-carboxylic ester; $\xrightarrow{H_2O}$ Butane-tetra-carboxylic acid $\xrightarrow[-CO_2]{Heat}$ Adipic acid

(5) **Synthesis of αβ-unsaturated acid.** Malonic ester undergoes Knoevenagel reaction with aldehydes in the presence of organic bases (*e.g.*, pyridine) and gives an unsaturated ester and finally an unsaturated acid.

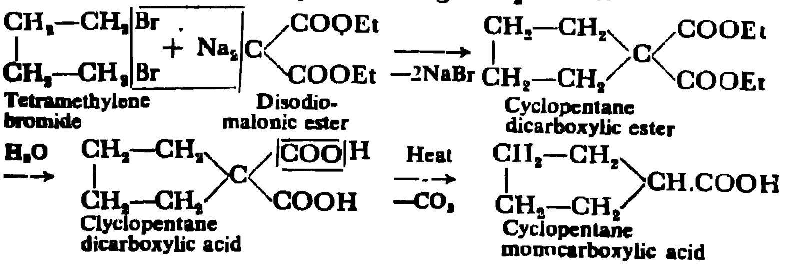
$$\underset{\text{Aldehyde}}{RCH=\overline{O+H_2}}\underset{\text{Malonic ester}}{C(COOEt)_2} \xrightarrow{\text{Pyridine}} \underset{\text{Unsaturated ester}}{RCH=C(COOEt)_2}$$



Unsaturated ester → Unsaturated dibasic acid → Unsaturated fatty acid

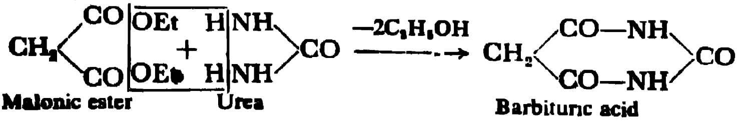
Malonic ester condenses with aldehydes only (*cf.* Acetoacetic and cyanoacetic esters).

(6) **Synthesis of cyclic or ring compounds.**



Tetramethylene bromide + Disodio-malonic ester → Cyclopentane dicarboxylic ester $\xrightarrow{H_2O}$ Clyclopentane dicarboxylic acid $\xrightarrow[-CO_2]{Heat}$ Cyclopentane monocarboxylic acid

(7) **Synthesis of Heterocyclic compounds.** Urea and malonic ester combine to form malonylurea or barbituric acid and alcohol.



Malonic ester + Urea → Barbituric acid

CYANOACETIC ESTER

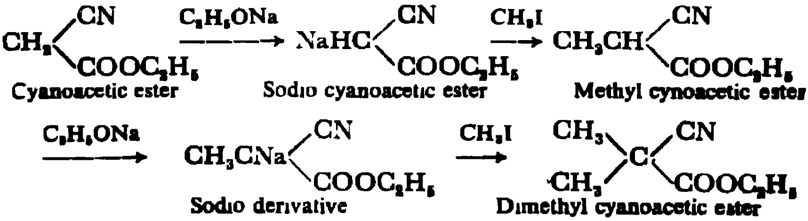
6. Cyanoacetic Ester or Ethyl Cyanoacetate, ($CN.CH_2.COOC_2H_5$.)

Preparation. Ethyl cyanoacetate is prepared by treating monochloroacetic acid with potassium cyanide when we get cyanoacetic acid, which being an acid, can be esterified to yield ethyl cyanoacetate. The process of esterification employed should be such that the cyanide group in the molecule is not hydrolysed during this process. This can be done by converting cyanoacetic acid into its acid chloride with phosphorus trichloride or pentachloride or thionyl chloride. The acid chloride so obtained is treated with ethyl alcohol when ethyl cyano acetate is obtained.

$$\underset{\text{Monochloro-acetic acid}}{\mathrm{Cl.CH_2COOH}} \xrightarrow{\mathrm{KCN}} \underset{\text{Cyanoacetic acid}}{\mathrm{CN.CH_2COOH}} \xrightarrow[\mathrm{SOCl_2}]{\mathrm{PCl_5\ or}} \underset{\text{Cyanoacetyl chloride}}{\mathrm{CN.CH_2COCl}}$$

$$\xrightarrow{\mathrm{C_2H_5OH}} \underset{\text{Ethyl cyanoacetate}}{\mathrm{CN.CH_2COOC_2H_5}}$$

Use of Cyanoacetic ester in the synthesis of organic compounds. In cyanoacetic ester ($\mathrm{CN{-}CH_2{-}COOC_2H_5}$), the methylene group ($\mathrm{-CH_2-}$) is situated between two electro-negative radicals $\mathrm{-CN}$ group and $\mathrm{-COOC_2H_5}$ group, and is, therefore, highly reactive. Like all other compounds (*e.g.*, malonic ester and acetoacetic ester containing a methylene group present between two negative groups) the hydrogen atoms of methylene group can be successively replaced by sodium when treated with sodium ethoxide.

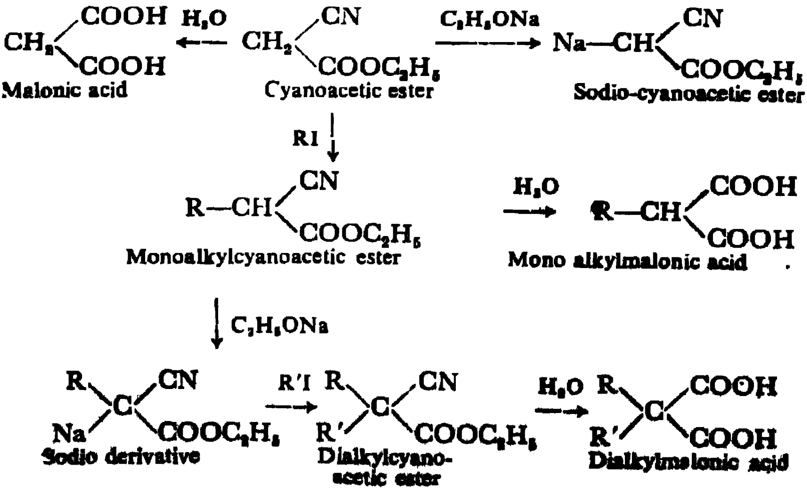


$$\underset{\text{Cyanoacetic ester}}{\mathrm{CH_2}\Big<\begin{array}{l}\mathrm{CN}\\ \mathrm{COOC_2H_5}\end{array}} \xrightarrow{\mathrm{C_2H_5ONa}} \underset{\text{Sodio cyanoacetic ester}}{\mathrm{NaHC}\Big<\begin{array}{l}\mathrm{CN}\\ \mathrm{COOC_2H_5}\end{array}} \xrightarrow{\mathrm{CH_3I}} \underset{\text{Methyl cynoacetic ester}}{\mathrm{CH_3CH}\Big<\begin{array}{l}\mathrm{CN}\\ \mathrm{COOC_2H_5}\end{array}}$$

$$\xrightarrow{\mathrm{C_2H_5ONa}} \underset{\text{Sodio derivative}}{\mathrm{CH_3CNa}\Big<\begin{array}{l}\mathrm{CN}\\ \mathrm{COOC_2H_5}\end{array}} \xrightarrow{\mathrm{CH_3I}} \underset{\text{Dimethyl cyanoacetic ester}}{\begin{array}{r}\mathrm{CH_3}\\ \mathrm{CH_3}\end{array}\Big>\mathrm{C}\Big<\begin{array}{l}\mathrm{CN}\\ \mathrm{COOC_2H_5}\end{array}}$$

Cyanoacetic ester is, therefore, an important synthesising agent used for the synthesis of a number of organic compounds as given below :

(1) **Synthesis of Malonic and Substituted malonic acids.**



$$\underset{\text{Malonic acid}}{\mathrm{CH_2}\Big<\begin{array}{l}\mathrm{COOH}\\ \mathrm{COOH}\end{array}} \xleftarrow{\mathrm{H_2O}} \underset{\text{Cyanoacetic ester}}{\mathrm{CH_2}\Big<\begin{array}{l}\mathrm{CN}\\ \mathrm{COOC_2H_5}\end{array}} \xrightarrow{\mathrm{C_2H_5ONa}} \underset{\text{Sodio-cyanoacetic ester}}{\mathrm{Na{-}CH}\Big<\begin{array}{l}\mathrm{CN}\\ \mathrm{COOC_2H_5}\end{array}}$$

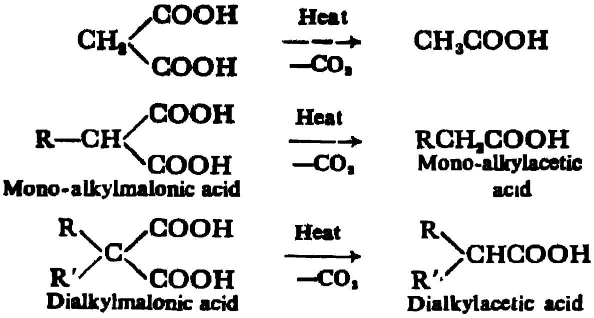
$$\Big\downarrow \mathrm{RI}$$

$$\underset{\text{Monoalkylcyanoacetic ester}}{\mathrm{R{-}CH}\Big<\begin{array}{l}\mathrm{CN}\\ \mathrm{COOC_2H_5}\end{array}} \xrightarrow{\mathrm{H_2O}} \underset{\text{Mono alkylmalonic acid}}{\mathrm{R{-}CH}\Big<\begin{array}{l}\mathrm{COOH}\\ \mathrm{COOH}\end{array}}.$$

$$\Big\downarrow \mathrm{C_2H_5ONa}$$

$$\underset{\text{Sodio derivative}}{\begin{array}{r}\mathrm{R}\\ \mathrm{Na}\end{array}\Big>\mathrm{C}\Big<\begin{array}{l}\mathrm{CN}\\ \mathrm{COOC_2H_5}\end{array}} \xrightarrow{\mathrm{R'I}} \underset{\text{Dialkylcyano-acetic ester}}{\begin{array}{r}\mathrm{R}\\ \mathrm{R'}\end{array}\Big>\mathrm{C}\Big<\begin{array}{l}\mathrm{CN}\\ \mathrm{COOC_2H_5}\end{array}} \xrightarrow{\mathrm{H_2O}} \underset{\text{Dialkylmalonic acid}}{\begin{array}{r}\mathrm{R}\\ \mathrm{R'}\end{array}\Big>\mathrm{C}\Big<\begin{array}{l}\mathrm{COOH}\\ \mathrm{COOH}\end{array}}$$

(2) **Synthesis of Fatty acids.** Malonic acid and its mono- or dialkyl derivatives, obtained above, lose CO_2 on heating and yield acetic acid and its mono- or dialkyl derivatives respectively.

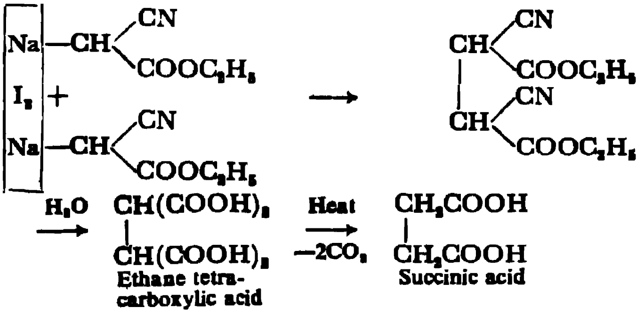


$$CH_2(COOH)_2 \xrightarrow[-CO_2]{Heat} CH_3COOH$$

$$R{-}CH(COOH)_2 \xrightarrow[-CO_2]{Heat} RCH_2COOH$$

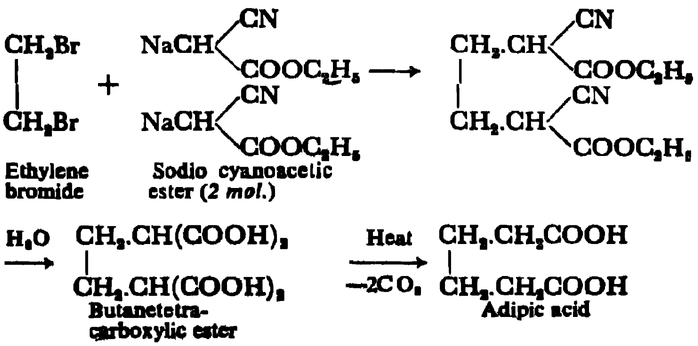
$$RR'C(COOH)_2 \xrightarrow[-CO_2]{Heat} RR'CHCOOH$$

(3) **Synthesis of Dibasic and other Polybasic acids.** Sodio cyanoacetic ester reacts with another molecule in the presence of iodine. The product on hydrolysis and subsequent heating yields succinic acid.



$$2\,Na{-}CH(CN)COOC_2H_5 + I_2 \longrightarrow CH(CN)COOC_2H_5{-}CH(CN)COOC_2H_5 \xrightarrow{H_2O} CH(COOH)_2{-}CH(COOH)_2 \xrightarrow[-2CO_2]{Heat} CH_2COOH{-}CH_2COOH$$

(4) **Synthesis of higher Dibasic acids.** Sodio cyanoacetic ester when treated with an alkylene halide or a polymethylene halide yields higher dibasic acids :

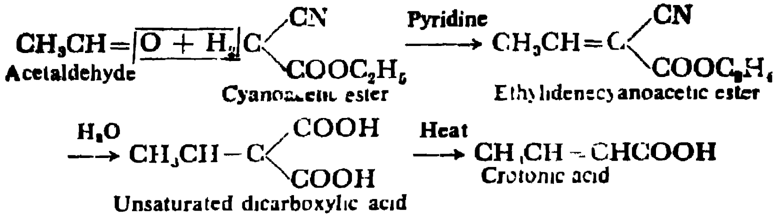


$$CH_2Br{-}CH_2Br + 2\,NaCH(CN)COOC_2H_5 \longrightarrow CH_2.CH(CN)COOC_2H_5{-}CH_2.CH(CN)COOC_2H_5 \xrightarrow{H_2O} CH_2.CH(COOH)_2{-}CH_2.CH(COOH)_2 \xrightarrow[-2CO_2]{Heat} CH_2.CH_2COOH{-}CH_2.CH_2COOH$$

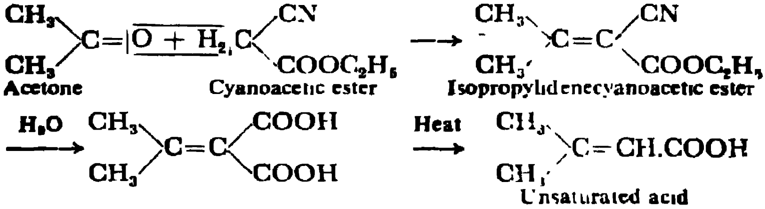
Ethylene bromide
Sodio cyanoacetic ester (2 *mol.*)
Butanetetra-carboxylic ester
Adipic acid

(5) **Synthesis of Unsaturated acids.** Cyanoacetic ester undergoes the *Knoevenagel reaction* with aldehyde in the presence of

a base (e.g., pyridine). The product on hydrolysis and heating gives **a β-unsaturated acid.**



It condenses with ketones as well in the presence of acetamide in glacial acetic acid solution provided the water formed is being continually removed by distillation.



QUESTIONS

Essay Type :

1. What do you understand by reactive methylene group ? Describe the synthetic uses of one compound containing a reactive methylene group
(Delhi B Sc. Hons. Sub 1977)

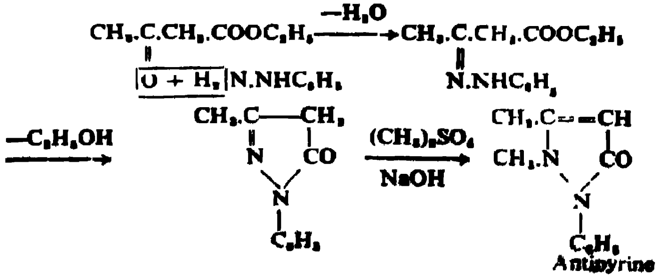
2. Describe the synthesis of acetoacetic ester and explain the mechanism of the reaction involved. Give its chemical properties Describe its importance in synthesis. *(Delhi B.Sc. 1974 ; Osmania 1971 ; Nagpur 1974 Supp ; Delhi B.Sc. Hons. 1976)*

3. Describe the preparation of acetoacetic ester. Discuss its constitution. How will you obtain any four of the following compounds by the use of acetoacetic ester ?

(*i*) Ethyl-propylacetic acid. (*ii*) Succinic acid. (*iii*) *n*-Butane
(*iv*) Methyl amyl ketone or methly propyl ketone or methyl *n*-butyl ketone
(*v*) Crotonic acid. (*vi*) 4-Methyluracil.
(*vii*) Antipyrine. (*viii*) 1 : 4-diketone.
(*ix*) Isobutyric acid and *n*-butyric acid. (*x*) Acetonylacetone.
(*xi*) Active valeric acid. (*xii*) Laevulinic acid.

(Delhi B.Sc. 1981 ; Delhi B.Sc. Hons. Sub. 1981)

[**Hint.** (*v*) Antipyrine is 2, 3-dimethyl-1-phenyl-pyrazol-5-one.



(*vi*) Acetonylacetone is a 1 : 4-diketone.

(*ix*) Ethylmethylacetic acid is active valeric acid.

(*x*) Laevulinic acid is β-acetylpropionic acid or γ-ketovaleric acid.]

4. (*a*) Discuss the constitution of acetoacetic ester.

(*b*) What is the evidence that it exists in two isomeric forms ?

(*c*) Discuss the isomerism exhibited by ethyl acetoacetate.

5. Discuss the preparation, properties and synthetic application of malonic ester. (*Utkal B.Sc. 1976* ; *Kurukshetra 1967* ; *Gorakhpur 1967*)

6. Describe the important stages in the preparation of ethyl malonate from acetic acid. Illustrate the use of compound in the preparation of :

(*a*) Propionic acid ; (*b*) Succinic acid ; (*c*) Barbituric acid ;
(*d*) $R_1R_2CH.COOH$; (*e*) $RCH{=}CH.COOH$; (*f*) Ethylsuccinic acid ;
(*g*) Dimethylacetic acid ; (*h*) 1 : 3-dimethylglutaric acid ;
(*i*) Ethyl methyl ketone ; (*j*) Crotonic acid ; (*k*) Acetoacetic acid.
(*Rajasthan B.Sc. 1966* ; *Utkal 1976* ; *Punjab 1970* ; *Delhi 1971*)

7. Describe the preparation of ethyl cyanoacetate. Illustrate by examples how this ester is used in the synthesis of organic compounds. Give reasons why ethyl cyanoacetate gives a sodium compound while ethyl acetate does not.

8. (*a*) How will you prepare a pure sample of diethyl malonate ?

(*b*) Starting from diethyl malonate how will you obtain the following :

(*i*) Dimethylacetic acid, (*ii*) Succinic acid,
(*iii*) Barbituric acid, (*iv*) Crotonic acid ?
(*Delhi B.Sc. 1978 Supp.*)

9. (*a*) Describe what happens when ethyl acetate is heated with sodium ethoxide in presence of ethyl alcohol.

(*b*) Explain how the product obtained by the above reaction can be used for the synthesis of—

(*i*) *n*-butyric acid, (*ii*) 4-methyluracil, and (*iii*) ethyl methyl ketone.
(*Delhi B.Sc. 1978*)

10. How is ethyl acetoacetate prepared ? Starting from ethyl acetoacetate how are the following prepared :

(*a*) ethyl methyl ketone,
(*b*) β-methylbutyric acid,
(*c*) methyl isopropyl ketone,
(*d*) methylsuccinic acid. (*Andhra B.Sc. 1978*)

Short Answer Type :

1. What is an active methylene group ? Give structures of three compounds having such a group. (*Delhi B.Sc. Hons. 1977* ; *B.Sc. 1976 Supp.*)

2. Why is the keto form of acetoacetic ester more stable than its enolic form ? (*Delhi B.Sc. Hons. 1977*)

3. How can the following compounds be prepared from *either* acetoacetic ester or malonic ester ?

(*i*) Benzylacetone, (*ii*) $CH_3COCH_2CH_2COOH$,
(*iii*) Barbituric acid, (*iv*) Glutaric acid.
(*Delhi B.Sc. Hons. 1977*)

4. How can malonic acid be converted into—

(*i*) crotonic acid, (*ii*) succinic acid,
(*iii*) barbituric acid, (*iv*) cyclopropane-carboxylic acid ?
(*Delhi B.Sc. 1976 Supp.*)

5. Discuss the isomerism exhibited by ethyl acetoacetate.
(*Nagpur B.Sc. 1974 Supp.*)

6. Ethyl acetoacetate decolorises bromine water. Give reason why.
(*Andhra B.Sc. 1978*)

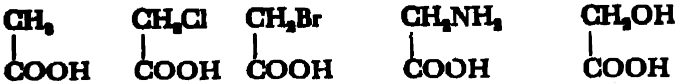
7. Explain the following fact :
Ethyl acetoacetate exists in two forms. (*Andhra B.Sc. 1978*)

8. How is diethyl malonate prepared in the laboratory ?
(*Madras B.Sc. 1978*)

31

Substituted Acids—I

1. **The Substituted Acids.**—The derivatives of carboxylic acids obtained by replacing one or more hydrogen atoms of the alkyl radical by different atoms or groups such as —Cl, —Br, $—NH_2$, —OH, etc., are called ***Substituted acids***. For example, from acetic acid, we get



$\begin{matrix} CH_3 \\ | \\ COOH \end{matrix}$ Acetic acid $\quad \begin{matrix} CH_2Cl \\ | \\ COOH \end{matrix}$ Chloroacetic acid $\quad \begin{matrix} CH_2Br \\ | \\ COOH \end{matrix}$ Bromoacetic acid $\quad \begin{matrix} CH_2NH_2 \\ | \\ COOH \end{matrix}$ Aminoacetic acid $\quad \begin{matrix} CH_2OH \\ | \\ COOH \end{matrix}$ Hydroxyacetic acid

The usual method of naming the substituted acids is to use the trivial names of the acids and to indicate the positions of the substituents by Greek letters. The carbon atom attached to the carboxyl group is termed the α-carbon, the next one as β-carbon, and so on.

$$\overset{\delta}{C}H_3—\overset{\gamma}{C}H_2—\overset{\beta}{C}H_2—\overset{\alpha}{C}H_2—COOH$$

Formula	*Name*
$CH_3CHCl.COOH$	α-chloropropionic acid
$CH_2OH.CH_2COOH$	β-hydroxypropionic acid

According to the IUPAC system of nomenclature, the positions of the substituents are indicated by numbers, *e.g.*,

$CH_3.CH_2.CHOH.COOH$ 2-hydroxybutanoic acid or 1-hydroxypropane-1-carboxylic acid

The substituted acids, as a rule, exhibit somewhat the properties of both the functional groups. Thus chloroacetic acid exhibits the properties of an alkyl halide as well as an acid. Similarly hydroxyacetic acid behaves both as an alcohol and as an acid. The properties of one functional group may, however, be considerably modified by the other. The chloroacetic acid is a stronger acid and glycine a weaker acid. We shall discuss in this chapter some typical members of substituted acids.

HALOGEN-SUBSTITUTED ACIDS

2. **Halogen-substituted Acids.**—These are derived from the acids by replacement of one or more hydrogen atoms of the alkyl group by halogen atoms. For example, three chloroacetic acids are :

$CH_2Cl.COOH$	$CHCl_2.COOH$	$CCl_3.COOH$
Monochloroacetic acid	Dichloroacetic acid	Trichloroacetic acid

General Methods of Preparation. The methods of preparation of halogen-substituted fatty acids differ with the position in which the halogen atom is to be substituted. In general they are prepared by the following methods :

(*i*) **Direct Halogenation.** A fatty acid is directly chlorinated or brominated by passing chlorine or bromine through the boiling fatty acid in the presence of sunlight and halogen carriers such as iodine, red phosphorus or sulphur. Whereas bromination takes place only at the α-position, chlorination, although it occurs mainly at the α-position, may also take place in the β-position and still further in the chain.

$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{Cl_2} \underset{\text{Monochloroacetic acid}}{CH_2ClCOOH} \xrightarrow{Cl_2} \underset{\text{Dichloroacetic acid}}{CHCl_2COOH} \xrightarrow{Cl_2} \underset{\text{Trichloroacetic acid}}{CCl_3COOH}$$

$$\underset{\text{Propionic acid}}{CH_3CH_2COOH} \xrightarrow{Cl_2} \underset{\alpha\text{-Chloropropionic acid}}{CH_3CHClCOOH} + \underset{\beta\text{-Chloropropionic acid}}{CH_2Cl.CH_2.COOH}$$

Direct halogenation of higher fatty acids is difficult. The usual method for preparing α-chloro or α-bromo acids is by the **Hell Volhard-Zelinsky reaction (HVZ reaction)**—*by treating acid with chlorine or bromine in the presence of a small amount of red phosphorus.* This reaction takes place probably as follows :

$$RCH_2.COOH \xrightarrow{P+Br_2} RCH_2.COBr \xrightarrow{Br_2} RCHBr.COBr$$

$$R.CHBr.COBr + R.CH_2COOH \rightleftharpoons RCHBr.COOH + RCH_2.COBr$$

$$RCH_2.COBr \xrightarrow{Br_2} R.CHBr.COBr, \text{ etc.}$$

The second α-hydrogen atom may be replaced by taking excess of the halogen. Bromination ceases after both α-hydrogen atoms have been replaced, chlorination proceeds further in the chain.

The HVZ reaction with bromine is applicable to dibasic and polybasic acids also.

(*ii*) **Iodination.** Direct iodination is not possible, so iodine-substituted fatty acids are prepared by treating corresponding chloro-derivative with potassium iodide or by addition of hydriodic acid to unsaturated acid [See (*iii*) below].

$$\underset{\text{Chloroacetic acid}}{CH_2ClCOOH} + KI \longrightarrow \underset{\text{Iodoacetic acid}}{CH_2I.COOH} + KCl$$

(*iii*) **From Unsaturated Acids.** A molecule of halogen acids may be added to unsaturated acids when a saturated halogenated acid is obtained. The halogen atom attaches to the carbon atom further away from the carboxylic group—this is an exception to the Markownikoff's rule.

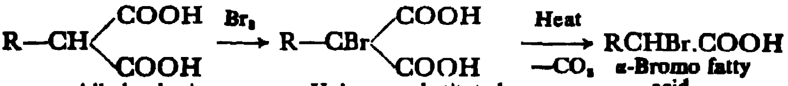
$$\underset{\text{Acrylic acid}}{CH_2{=}CH.COOH} + HI \longrightarrow \underset{\beta\text{-iodopropionic acid}}{CH_2ICH_2COOH}$$

This mode of addition may be ascribed to the inductive effect of the carboxyl group (*cf.* allyl alcohol). On the other hand, addition of halogen acid to γδ-unsaturated acids, *e.g.*,

$$\mathrm{CH_2{=}CH.CH_2.CH_2.COOH} \xrightarrow{\mathrm{HCl}} \mathrm{CH_3.CHCl.CH_2.CH_2COOH}$$

takes place in accordance with Markownikoff's rule. This must be due to the fact that the inductive effect of the carboxyl group ceases to be felt beyond the β-carbon atom.

(*iv*) **From alkylmalonic acids.**



$$\mathrm{R{-}CH}\begin{matrix}\diagup\mathrm{COOH}\\ \diagdown\mathrm{COOH}\end{matrix} \xrightarrow{\mathrm{Br_2}} \mathrm{R{-}CBr}\begin{matrix}\diagup\mathrm{COOH}\\ \diagdown\mathrm{COOH}\end{matrix} \xrightarrow[\mathrm{-CO_2}]{\text{Heat}} \mathrm{RCHBr.COOH}$$

Alkylmalonic acid — Halogen-substituted alkylmalonic acid — α-Bromo fatty acid

(*v*) **From Hydroxyacids.** Hydroxyacids are treated with phosphorus halide and halogenated acid produced is hydrolysed with water.

$$\underset{\substack{\text{Hydroxyacetic}\\\text{acid}}}{\mathrm{CH_2(OH)COOH}} \xrightarrow{\mathrm{PCl_5}} \underset{\substack{\text{Chloro-acetyl}\\\text{chloride}}}{\mathrm{CH_2ClCOCl}} \xrightarrow{\mathrm{H_2O}} \underset{\substack{\text{Chloroacetic}\\\text{acid}}}{\mathrm{CH_2ClCOOH}}$$

General Properties : Physical. These are colourless liquids or solids which dissolve in water giving strongly acidic solution.

Chemical. Halogen-substituted fatty acids, as a rule, possess more or less the characteristics of both the groups, *viz.*, halogen atom and —COOH group, present in the molecule. As will be clear from the following properties, they behave both as an alkyl halide and a fatty acid.

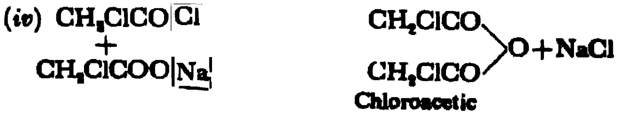
(1) **Reactions of the carboxyl group.** Just like ordinary fatty acids they give rise to salts, esters, and chlorides, acid anhydrides, etc.

(*i*) $\underset{\substack{\text{Chloroacetic}\\\text{acid}}}{\mathrm{2CH_2ClCOOH}} + \mathrm{Na_2CO_3} \longrightarrow \underset{\substack{\text{Sodium chloro-}\\\text{acetate}}}{\mathrm{2CH_2ClCOONa}} + \mathrm{CO_2} + \mathrm{H_2O}$

(*ii*) $\underset{\text{Chloroacetic acid}}{\mathrm{CH_2ClCO}|\underline{\overline{\mathrm{OH\ +\ H}}}|}\underset{\text{Ethyl alcohol}}{\mathrm{OC_2H_5}} \longrightarrow \underset{\text{Ethyl chloroacetate}}{\mathrm{CH_2ClCOOC_2H_5}} + \mathrm{H_2O}$

(*iii*) $\underset{\substack{\text{Chloroacetic}\\\text{acid}}}{\mathrm{CH_2ClCOOH}} + \mathrm{PCl_5} \longrightarrow \underset{\substack{\text{Chloroacetyl}\\\text{chloride}}}{\mathrm{CH_2ClCOCl}} + \mathrm{POCl_3} + \mathrm{HCl}$

(*iv*)



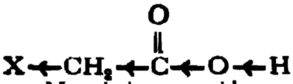
$$\begin{matrix}\mathrm{CH_2ClCO}|\overline{\mathrm{Cl}}\\ +\\ \mathrm{CH_2ClCOO}|\underline{\mathrm{Na}}|\end{matrix} \qquad \begin{matrix}\mathrm{CH_2ClCO}\diagdown\\ \\ \mathrm{CH_2ClCO}\diagup\end{matrix}\mathrm{O} + \mathrm{NaCl}$$

Chloroacetic anhydride

The halogen-substituted acids are stronger than the fatty acids. Chloro-acids are stronger than bromo-acids which are stronger than iodo-acids. Similarly, tri-halogeno-acids (*e.g.*, $\mathrm{CCl_3COOH}$) are stronger than dihalogeno-acids (*e.g.*, $\mathrm{CHCl_2COOH}$), which are stronger than monohalogeno-acids ($\mathrm{CH_2ClCOOH}$). α-substituted

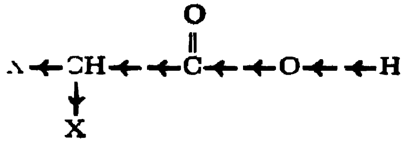
acids are stronger than β-substituted acids which in turn are stronger than γ-substituted acids.

The increase in acid strength of halogeno-acids may be explained by the high electron affinity of the halogen atom which exerts a strong inductive effect, thereby facilitating the release of proton from the carboxyl group. The larger the number of halogen atoms on the α-carbon atom, the stronger the inductive effect and consequently the stronger is the acid. This explains why trihalogeno-acid is stronger than the dihalogeno-acid which in turn is stronger than the mono-halogeno-acid.



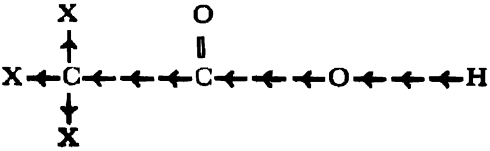
$$X \leftarrow CH_2 \leftarrow \overset{\overset{O}{\|}}{C} \leftarrow O \leftarrow H$$

Monohalogeno-acid



$$X \leftarrow \underset{\underset{X}{\downarrow}}{CH} \leftarrow\leftarrow \overset{\overset{O}{\|}}{C} \leftarrow\leftarrow O \leftarrow\leftarrow H$$

Dihalogeno-acid



$$X \leftarrow \overset{\overset{X}{\uparrow}}{\underset{\underset{X}{\downarrow}}{C}} \leftarrow\leftarrow\leftarrow \overset{\overset{O}{\|}}{C} \leftarrow\leftarrow\leftarrow O \leftarrow\leftarrow\leftarrow H$$

Trihalogeno-acid

The farther removed the halogen atom is from the carboxyl group, the weaker is the inductive effect at carboxyl group, and consequently weaker is the acid. This explains why α-substituted acids are stronger than β-substituted acids which in turn are stronger than γ-substituted acids.

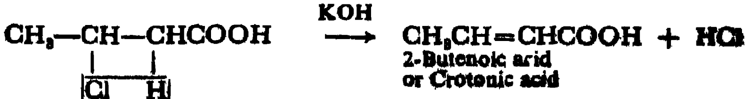
(2) **Reactions of the halogen atom.** The halogen atom can be replaced by —OH, —CN, $—NH_2$, $—NO_2$ and other groups just as in alkyl halides.

See Reactions of Monochloroacetic acid on page 2·355.

(3) **Distinctive properties of α-, β-, and γ-halogeno-acids.** In some reactions the final product is not the same when α-, β-, and γ-acids are separately treated with the same reagent as will be clear from the following examples when α-, β- and γ-chlorobutyric acids are boiled with an aqueous KOH solution.

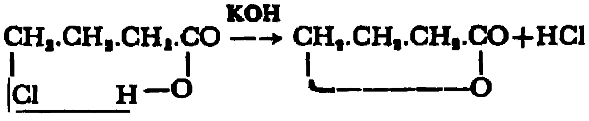
$$CH_3CH_2CHClCOOH + KOH \longrightarrow CH_3CH_2CH(OH)COOH + KCl$$

α-Chlorobutyric acid   α-hydroxy-butyric acid



$$CH_3-\underset{\boxed{Cl}}{CH}-\underset{\boxed{H}}{CH}COOH \xrightarrow{KOH} CH_3CH{=}CHCOOH + HCl$$

β-Chlorobutyric acid   2-Butenoic acid or Crotonic acid



$$CH_2.CH_2.CH_2.CO(Cl)(OH) \xrightarrow{KOH} CH_2.CH_2.CH_2.CO(O) + HCl$$

γ-Chlorobutyric acid γ-Butyrolactone

Thus we find that while in α-chloro acid, the chlorine atom is simply replaced by —OH group, the β- and γ-acids lose one molecule of HCl to produce an unsaturated acid and a lactone respectively. This behaviour can be used as a method of distinction between α-, β-, and γ-substituted halogeno-acids.

3. Monochloroacetic acid, $CH_2Cl.COOH$.—Monochloroacetic acid may be prepared *by passing chlorine through boiling glacial acetic acid in direct sunlight and in the absence of red phosphorus.*

$$CH_3COOH + Cl_2 \xrightarrow{\text{Sunlight}} CH_2Cl.COOH + HCl$$

It may be prepared industrially by agitating trichloroethylene with 90 per cent sulphuric acid.

$$\underset{\text{Trichloroethylene}}{CHCl{=}CCl_2} + 2H_2O \xrightarrow{H_2SO_4} \underset{\text{Monochloroacetic acid}}{CH_2Cl.COOH} + 2HCl$$

Properties. Monochloroacetic acid is a deliquescent solid (m.p. 334K), soluble in water and alcohol. It has a corrosive action on the skin.

Chemically it is far stronger than acetic acid and gives the reactions of both methyl chloride and acetic acid.

(*a*) *Reactions similar to Acetic acid.* Like acetic acid it reacts with metals, metal carbonates, alkalis, alcohols and phosphorus halides.

$$2CH_2Cl.COOH + 2Na \rightarrow \underset{\text{Sod. chloroacetate}}{2CH_2ClCOONa} + H_2$$

$$CH_2Cl.COOH + C_2H_5OH \rightarrow \underset{\text{Ethyl chloroacetate}}{CH_2Cl.COOC_2H_5} + H_2O$$

$$\underset{\text{Chloroacetic acid}}{CH_2Cl.COOH} + PCl_5 \rightarrow \underset{\text{Chloroacetyl chloride}}{CH_2Cl.COCl} + POCl_3 + HCl$$

(*b*) *Reactions similar to Methyl chloride.* Just as in methyl chloride, the chlorine atom in chloroacetic acid can be replaced by —OH, —CN, —NH_2, —NO_2, etc.

(*i*) On heating with aqueous potash or moist silver oxide, glycollic acid is formed.

$$\underset{\text{Chloroacetic acid}}{CH_2Cl.COOH} + \underset{\text{Moist silver oxide}}{AgOH} \rightarrow \underset{\text{Glycollic acid or Hydroxyacetic acid}}{CH_2OH.COOH} + AgCl$$

(*ii*) With potassium cyanide, cyanoacetic acid is obtained.

$$CH_2Cl.COOH + KCN \rightarrow CH_2(CN)COOH + KCl$$

(*iii*) Glycine is obtained with alcoholic ammonia.

$$CH_2Cl.COOH + 2NH_3 \rightarrow \underset{\text{Aminoacetic acid or Glycine}}{CH_2NH_2.COOH} + NH_4Cl$$

(*iv*) With silver nitrite, nitroacetic acid is formed.

$$CH_2Cl.COOH + AgNO_2 \rightarrow CH_2NO_2COOH + AgCl$$

(*v*) Iodoacetic acid is obtained with potassium iodide.

$$CH_2ClCOOH + KI \rightarrow CH_2ICOOH + KCl$$

Uses. Monochloroacetic acid finds many uses in organic syntheses.

4. **Dichloroacetic acid, $CHCl_2COOH$.**—It may be prepared by adding calcium carbonate to a warm aqueous solution of chloral hydrate and then adding sodium cyanide solution and heating the mixture.

$$2CCl_3.CH(OH)_2 + 2CaCO_3 \xrightarrow{NaCN} (CHCl_2COO)_2Ca + 2CO_2 + CaCl_2 + 2H_2O$$

Dichloroacetic acid is generated by acidifying the mixture.

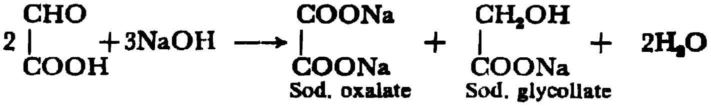
$$(CHCl_2.COO)_2Ca + 2HCl \longrightarrow 2CHCl_2COOH + CaCl_2$$

The function of sodium cyanide is not clear.

It is a colourless liquid (b.p. 467K). On careful hydrolysis with dilute alkali it gives glyoxylic acid.

$$CHCl_2.COOH + H_2O \xrightarrow{\text{Dil. NaOH}} CHO.COOH + 2HCl$$

On vigorous hydrolysis with concentrated alkali, glyoxylic acid produced undergoes Cannizzaro reaction to give oxalate and glycollate.



$$2\begin{array}{c}CHO\\|\\COOH\end{array} + 3NaOH \longrightarrow \underset{\text{Sod. oxalate}}{\begin{array}{c}COONa\\|\\COONa\end{array}} + \underset{\text{Sod. glycollate}}{\begin{array}{c}CH_2OH\\|\\COONa\end{array}} + 2H_2O$$

5. **Trichloroacetic acid, $CCl_3.COOH$.**—It can be prepared by oxidising chloral hydrate with concentrated nitric acid.

$$CCl_3.CH(OH)_2 + [O] \xrightarrow{HNO_3} CCl_3COOH + H_2O$$

It is a colourless, deliquescent solid (m.p. 331K) and is one of the strongest organic acids. It gives chloroform when boiled with dilute alkali or even water.

$$CCl_3.COOH \longrightarrow CHCl_3 + CO_2$$

The C—C linkage breaks readily due to the presence of three electronegative chlorine atoms on the carbon atom adjacent to carbonyl group.

AMINO ACIDS

6. **Amino acids.**—Proteins are complex nitrogenous substances which occur in plants and in most cells of animal body. Proteins on hydrolysis with strong inorganic acids or by enzymes yield a mixture of amino acids. In all about twenty-five amino acids are known of which ten are essential, *i.e.*, a deficiency of any of these prevents growth in young animals, and may even cause death.

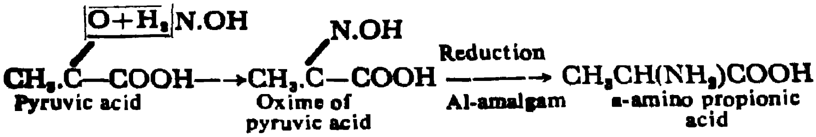
General Methods of Preparation of Amino acids.

(*i*) **From** halogen-substituted acids, by treating them with **ammonia** or potassiophthalimide (*Gabriel phthalimide reaction*).

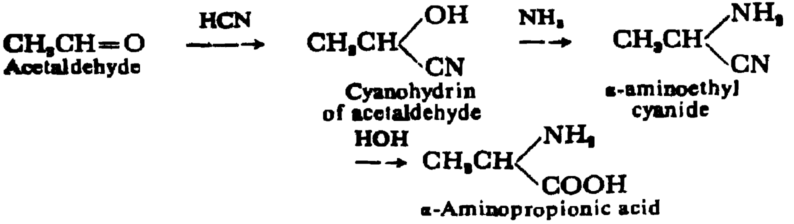
$$\underset{\text{Chloroacetic acid}}{CH_2ClCOOH} \xrightarrow{NH_3} \underset{\text{Aminoacetic acid}}{CH_2(NH_2)COOH} \xrightarrow[\text{reactions}]{\text{Secondary}} \underset{\text{Secondary amino acid}}{NH(CH_2COOH)_2} + \underset{\text{Tertiary amino acid}}{N(CH_2COOH)_3}$$

To avoid these secondary reactions the Gabriel's phthalimide synthesis is generally used (*see under Glycine*).

(*ii*) **By reduction of the oximes of aldehydic and ketonic acid.**



(*iii*) **Strecker's Method.** Starting with aldehydes and ketones aminoacids can be synthesised as follows :



(*iv*) **From Proteins.** Proteins on hydrolysis, by heating the with Ba $(OH)_2$ at 473K in an autoclave, produce a mixture of amino acids. This mixture on esterification gives a mixture of esters which can be separated by fractional distillation. The esters or hydrolysis give the corresponding aminoacids.

General Properties : Physical. Most of the amino acids are crystalline substances having high melting points and are sweet in taste. Simpler acids are readily soluble in water, higher members are less so. They are insoluble in alcohol and ether. Except glycine, all are optically active, some being dextro-rotatory while others laevo-rotatory. They give a deep red coloration with ferric chloride.

Chemical. The structure of the amino acids suggests that these compounds should behave both as acids and bases (amphoteric in nature). For example in an aqueous solution of glycine we have the following equilibria :

$$H_3\overset{+}{N}-CH_2COOH \underset{H_3O^+}{\overset{OH^-}{\rightleftharpoons}} \underset{\text{Zwitterion}}{H_3\overset{+}{N}-CH_2COO} \underset{H_3O^+}{\overset{OH^-}{\rightleftharpoons}} H_2NCH_2COO^-$$

$$\updownarrow$$

$$\underset{\text{neutral amino acid}}{H_2N-CH_2COOH}$$

The position of the equilibrium, however, depends on the pH of the solution. The dipolar ion is termed *zwitterion*. That α-amino acids actually exist as zwitterions is confirmed by their physical properties. These are generally soluble in water and have high melting points (*characteristics of ionic species*).

The acid centre in the zwitterion is the ammonium ion ($-NH_3^+$) rather than the free —COOH group. Similarly the basic centre is the carboxylate ion ($-COO^-$) rather than the free $-NH_2$ group. Acidity constant, K_a for glycine$=1{\cdot}6\times10^{-10}$ and basicity constant, $K_b=2{\cdot}5\times10^{-12}$. Low values of K_a and K_b are consistent with its zwitterion character.

In general, aminoacids combine in them the properties of amines and fatty acids are shown by the following reactions :

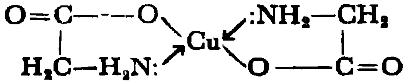
(*a*) **REACTIONS OF THE —COOH GROUP**

(*i*) Due to the presence of —COOH, they possess an acidic nature but due to the presence of the basic amino group they are *neutral towards litmus*.

(*ii*) With alkalis they produce salts on neutralisation.

$$CH_2(NH_2)COO\boxed{H + HO}K \longrightarrow CH_2(NH_2)COOK + H_2O$$

(*iii*) With copper salts glycine gives deep blue colour due to the formation of a compelx as a result of coordination with the amino group.



(*iv*) When heated with soda lime, they decompose into amine. .

$$\underset{\text{Glycine}}{CH_2(NH_2)COOH} \xrightarrow[\text{heat}]{\text{Soda lime}} \underset{\text{Methylamine}}{CH_3NH_2} + CO_2$$

(*b*) **REACTIONS OF THE AMINO GROUP**

(*i*) **Salt formation with acids.**

$$\underset{\text{Glycine}}{CH_2(NH_2)COOH} + HCl \longrightarrow \underset{\text{Glycine hydrochloride}}{CH_2(NH_2.HCl)\ COOH}$$

(*ii*) **Action of nitrous acid.**

$$\underset{\text{Glycine}}{\begin{array}{l|l|l} H_2 & N & -CH_2COOH \\ O & N & \ \ HO \end{array}} \longrightarrow \underset{\text{Glycollic acid}}{CH_2(OH)COOH} + N_2 + H_2O$$

(*iii*) **Acylation.** With acid chlorides, the H-atom of the $-NH_2$ group is replaced by an acyl group.

$$CH_2(NH_2)COOH + RCOCl \longrightarrow CH_2(NH.COR)COOH + HCl$$

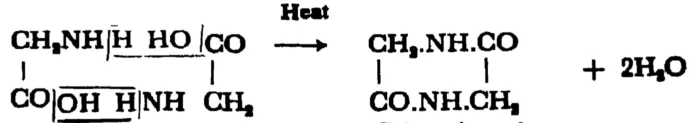
$$\underset{\text{Glycine}}{CH_2(NH_2)COOH} + \underset{\text{Acetyl chloride}}{CH_3COCl} \longrightarrow \underset{\text{Acetylglycine}}{CH_2(NH.COCH_3)COOH} + HCl$$

(*iv*) **Alkylation.** With alkyl halides, the hydrogen atoms are successively replaced by alkyl groups.

$$\underset{\text{Glycine}}{H_2N.CH_2COOH} \xrightarrow{CH_3I} \underset{\text{Methylglycine}}{CH_3NH.CH_2COOH} \xrightarrow{CH_3I} \underset{\text{Dimethylglycine}}{(CH_3)_2N.CH_2COOH}$$

(*c*) *Distinctive properties of α-, β-, and γ-Amino acids.* Intramolecular reactions of the amino acids on heating depend upon the positions of the amino group in the molecule with respect to carboxyl group, as will be clear from the following examples :

(*i*) ***α-amino acids*** give rise to cyclic anhydrides by losing water.



Two molecules of glycine Diketopiperazine

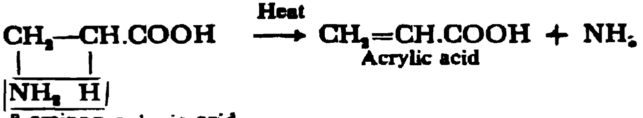
Diketopiperazine on partial hydrolysis gives a dipeptide of glycine.

$$H_2N—CH_2—\boxed{CONH}—CH_2—COOH$$

Peptide linkage

Peptides are compounds obtained by linking of COOH group of one amino acid with NH_2 group of the other. The CONH group linking the two molecules is termed *peptide linkage*.

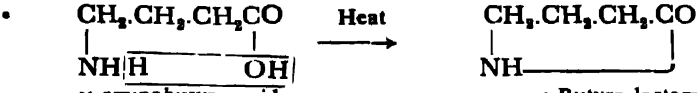
(*ii*) ***β-amino acids*** readily produce unsaturated acids with the loss of ammonia.



Acrylic acid

β-aminopropionic acid

(*iii*) ***γ-amino acids*** readily give rise to inner anhydrides known as lactams with the loss of a molecule of water.



γ-aminobutyric acid γ-Butyro-lactam

δ-amino acids and others having longer chains behave similar to γ-amino acids.

Analysis of α-Amino Acids. Chemically α-amino acids can be distinguished from amines by *ninhydrin test*. A solution of an α-amino acid on heating with ninhydrin, produces an intense blue-violet colour.

We can distinguish between individual amino acids by their **isoelectric points**. We have read earlier about the equilibrium which exists in an aqueous solution of glycine. This equilibrium suggests the following :

(*i*) At a lower *p*H (*i.e.*, in more acidic solution), the conjugate acid of glycine, given below, predominates.

$$H_3\overset{+}{N}—CH_2.COOH$$

Conjugate acid of glycine

(*ii*) At a higher *p*H (*i.e.*, in alkaline solution), the conjugate base of glycine, given below, will predominate.

$$H_2N—CH_2COO^-$$

Conjugate base of glycine

In an electric field, these ions will be seen migrating to the oppositely charged poles. At some intermediate pH, however, no such migration of ions takes place. This is because at this pH, electrically neutral zwitterions dominate the equilibrium and these are not attracted by any pole in an electric field.

This intermediate pH at which electrically neutral zwitterions dominate the equilibrium and there is no migration, is termed **isoelectric point.**

Each amino acid has a characteristic isoelectric point (Table 31·1). Thus an unknown amino acid can be identified from its isoelectric point.

Table 31·1—Isoelectric Points of some Amino acids

Name	*Formula*	*Isoelectric point*
Glycine	$H_2N—CH_2COOH$	6·0
Alanine	$CH_3.CH(NH_2).COOH$	6·0
Cysteine	$HS.CH_2.CH(NH_2)COOH$	5·1
Aspartic acid	$HOOC.CH_2.CH(NH_2).COOH$	2·8
Lencine	$(CH_3)_2CH.CH(NH_2)COOH$	6·0
Lysine	$H_2N(CH_2)_4.CH(NH_2)COOH$	9·6
Phenylalanine	$C_6H_5.CH_2.CH(NH_2)COOH$	5·5
Serine	$HOCH_2.CH(NH_2)COOH$	5·7

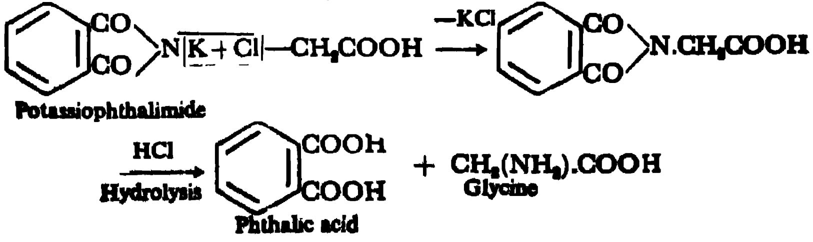
7. **Glycine (aminoacetic acid, glycocoll), $CH_2(NH_2)COOH$.** —It is the simplest amino acid which occurs in many proteins and certain animal excretions. For example, in combined state it is present in horse's urine as hippuric acid.

Preparation. It was originally obtained by boiling glue or gelatine with dilute mineral acid or alkali and has a sweet taste. On this account, it was named glycocoll (*glukus*=sweet ; *kolla*=glue).

It may be readily obtained by treating chloroacetic acid with a concentrated ammonium hydroxide solution.

$$CH_2Cl.COOH+2NH_3 \rightarrow \underset{\text{Glycine}}{CH_2(NH_2)COOH}+NH_4Cl \quad (64\text{-}65\%)$$

A pure sample of glycine may also be prepared by *Gabriel's phthalimide synthesis.* This phthalimide is converted into potassiophthalimide by treating with alcoholic potash. This is heated with chloroacetic acid and the product is hydrolysed by heating with 20% hydrochloric acid under pressure or refluxing with caustic potash solution when glycine and phthalic acid are obtained.



Properties : Physical. Glycine crystallizes as white prisms which melt, with decomposition, at 555-560K. It is readily soluble in water but insoluble in alcohol and ether. It has a sweet taste and gives a deep red coloration with ferric chloride.

Chemical. It is a typical amino acid and gives all the general reactions of the amino acids given before.

Sorensen formal titration. Glycine cannot be directly titrated with an alkali due to its amphoteric character. It can, however, be titrated if formaline solution is added to glycine before titration. Glycine gives methyleneglycine with formaline solution.

$$H_2NCH_2COOH+HCHO \longrightarrow \underset{\text{(an aldimine)}}{CH_2=NCH_2COOH}+H_2O$$

In methyleneglycine the basic character of an amino group has been suppressed, it is, therefore, a strong acid which can be titrated with sodium hydroxide using phenolphthalein as indicator. This method of titration is known as the *Sorensen formal titration.*

Uses. Glycine finds use in photography, medicine and in the manufacture of resins and varnishes.

QUESTIONS

Essay Type :

1. Discuss the general methods of preparation and general properties of halogen-substituted acids.

2. What methods would you suggest for the preparation of glycine ? What properties would it possess ? Give its important reactions.

3. Give an account of the methods available for the synthesis of aliphatic amino acids. What is their physiological importance and what light do they throw on the structure of proteins ? (*Agra B.Sc. 1973* ; *Jabalpur 1976*)

4. Give an account of the preparation of amino acids from natural sources and synthetic methods. Describe effect of heat on alpha, beta, and gamma-amino acids.

5. State giving equations some of the chemical properties of amino acids in which (*a*) only amino group is involved, (*b*) only carboxyl group is involved, and (*c*) both of the groups are involved simultaneously. (*Kanpur B.Sc. 1971*)

Short Answer Type :

1. What is the action of alkali on :

(*i*) Mono-, di- and trichloroacetic acids.

(*ii*) α-, β- and γ-chlorobutyric acids.

2. Write a note on relative strength of acetic acid and trichloroacetic acid in terms of inductive effect (explanation is required).

3. Write chemical equations for reaction between :

(1) Trichloroacetic acid+Dilute alkali (boil).

(2) Potassio phthalimide+chloroacetic ester followed by hydrolysis.

(3) Oxime of pyruvic acid+Al amalgam.

(4) Cyanohydrin of acetaldehyde+NH_3—followed by hydrolysis.

(5) Glycine+(*i*) NaOH ; (*ii*) $CuCO_3$; (*iii*) Soda-lime ; (*iv*) HCl ; (*v*) HONO ; (*vi*) CH_3COCl ; (*vii*) CH_3I.

(6) Action of heat on (*i*) Glycine ; (*ii*) β-aminopropionic acid ; (*iii*) aminobutyric acid.

4. Write equations for the following reactions :

(1) Alkylmalonic acid on bromination followed by heat.

(2) Hydroxyacetic acid+PCl_5 (followed by hydrolysis).

(3) Monochloroacetic acid+(*i*) Na ; (*ii*) Ethanol ; (*iii*) PCl_5 ; (*iv*) Moist silver oxide ; (*v*) KCN ; (*vi*) Alcoholic ammonia ; (*vii*) $AgNO_3$; (*viii*) KI.

(4) Heating chloroacetyl chloride with sodium chloroacetate.

(5) Action of heat on α-, β- and γ-chlorobutyric acids.

(6) Chloral hydrate+(*i*) $CaCO_3$ and NaCN ; (*ii*) Conc. HNO_3.

(7) Dichloroacetic acid (*i*) on careful hydrolysis with dilute alkali ; (*ii*) vigorous hydrolysis with conc. alkali.

5. What happens when—

(*i*) Trichloroacetic acid is heated with soda lime.

(*ii*) Formaldehyde is reacted with ammonia. (*Jabalpur B.Sc. 1976*)

6. What do you understand from isoelectric point ? (*Jabalpur B.Sc. 1976*)

7. Trichloroacetic acid is a very strong acid. Explain why. (*Calicut B.Sc. 1975*)

8. Describe any three methods for preparing amino acids. (*Agra B.Sc. 1973*)

9. How would you prove the amphoteric behaviour of amino acids ? (*Agra B.Sc. 1973*)

10. What is the action of heat on glycine ? (*Agra B.Sc. 1973*)

11. Monochloroacetic acid is a stronger acid than monobromoacetic acid. Explain why. (*Madras B.Sc. 1976 October*)

12. Trichloroacetic acid is a stronger acid than acetic acid. (*Madras B.Sc. 1976 Sept.*)

13. Explain why proteins in solution at low *p*H will migrate towards the cathode while in solutions of high *p*H these proteins migrate towards the anode. (*Bangalore B.Sc. 1974*)

14. Chloroacetic acid is a better proton donor compared to acetic acid. Give satisfactory explanation for this fact. (*Osmania B.Sc. 1975*)

15. How can a β-amino acid be obtained from : (*i*) an aldehyde, and (*ii*) a halogen-substituted acid ? (*Delhi B.Sc. 1976 Supp.*)

16. What are the substituted acids ? Give any three examples of substituted acids.

17. Which is more acidic : acetic acid or monochloroacetic acid ? Explain, why ?

18. How do you prepare glycine by Gabriel's phthalimide synthesis ?

19. What is a zwitterion ? Give names of two compounds which form a zwitterion.

20. Write the formula of the zwitterion given by glycine. Point out the acid and basic centre in it.

21. What predominates in the aqueous solution of glycine. (*i*) at lower *p*H (*i.e.*, more acidic solution) and (*ii*) at higher *p*H (*i.e.*, in alkaline solution) ?

22. Why does glycine give deep blue solution with copper salts ?

23. Is ethyl ester of glycine distinctly acidic or basic ? Give reasons.

24. What happens when glycine is heated ?

25. What happens on partial hydrolysis of diketopiperazine ? What is a peptide linkage ?

26. What is Sorensen formal titration ?

27. Can glycine be estimated by titration with a standard alkali ? Give reasons.

28. Chloroacetic acid is a better proton donor compared to acetic acid. Give satisfactory explanation for this fact.

29. Explain why glycine behaves both as an acid and a base. (*Delhi B.Sc. 1978*)

32

Substituted Acids—II

1. Hydroxy acids.—These are derived from acids by replacing one or more hydrogen atoms of the hydrocarbon radical by corresponding number of hydroxyl groups. A few common hydroxy acids are :

$CH_2OH.COOH$	Hydroxyacetic acid or Glycollic acid
$CH_3.CHOH.COOH$	α-Hydroxypropionic acid or Lactic acid
$CH_2OH.CH_2.COOH$	β-Hydroxypropionic acid or Hydracrylic acid
$CHOH.COOH$ $\vert$ $CH_2.COOH$	Monohydroxysuccinic acid or Malic acid
$CHOH.COOH$ $\vert$ $CHOH.COOH$	Dihydroxysuccinic acid or Tartaric acid
$CH_2.COOH$ $\vert$ $C(OH).COOH$ $\vert$ $CH_2.COOH$	2-Hydroxypropane-1, 2, 3-tricarboxylic acid or Citric acid

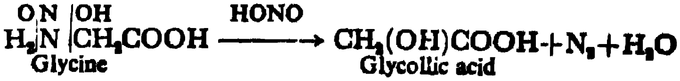
2. General Methods of Preparation of Hydroxy acids.—Hydroxy acids contain the two characteristic groups, the —OH and the —COOH groups, and can be prepared by introducing one of them into the molecule in which the other is already present, introducing both in case none is already present. The following methods will make it clear :

(*a*) *Introduction of —OH group when —COOH group is already present.*

(*i*) By boiling the chloro-acid with dilute alkali, moist silver oxide, or sodium carbonate solution.

$$\underset{\text{Chloroacetic acid}}{CH_2ClCOOH} + AgOH \longrightarrow \underset{\text{Glycollic acid}}{CH_2(OH)COOH} + AgCl$$

(*ii*) By treating the amino acids with nitrous acid (Sodium nitrite and dilute mineral acid).



$$\underset{\text{Glycine}}{\overset{ON\,|OH}{H_2N\,|CH_2COOH}} \xrightarrow{HONO} \underset{\text{Glycollic acid}}{CH_2(OH)COOH} + N_2 + H_2O$$

(*iii*) By reduction of aldehydic and ketonic acid.

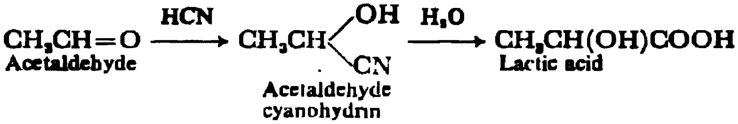
$$\underset{\text{Pyruvic acid}}{CH_3CO.COOH} \xrightarrow{2H} \underset{\text{Lactic acid}}{CH_3CH(OH)COOH}$$

(b) ***Introduction of —COOH group when —OH group is already present*, e.g., by oxidation of polyhydric alcohols, etc.**

$$\underset{\text{Ethylene glycol}}{CH_2(OH).CH_2OH} \xrightarrow[\text{dil. } HNO_3]{O} \underset{\text{Glycollic acid}}{CH_2(OH)COOH}$$

$$\underset{\text{Aldol}}{CH_3CH(OH).CH_2CHO} \xrightarrow{O} \underset{\beta\text{-hydroxybutyric acid}}{CH_3CH(OH)CH_2COOH}$$

(c) *Introduction of both —OH and —COOH groups when none is already present.* Cyanohydrins obtained from aldehydes and ketones give hydroxyacids on hydrolysis, e.g.,

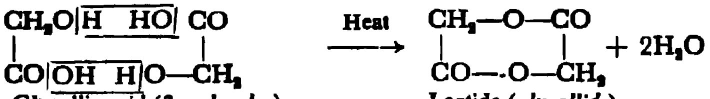


3. **General Properties** : **Physical.**—These are colourless crystalline solids or syrupy liquids extremely soluble in water but less soluble in alcohol and ether. Their melting and boiling points are much higher than those of parent acids. They are stronger acids as compared with their parent acids.

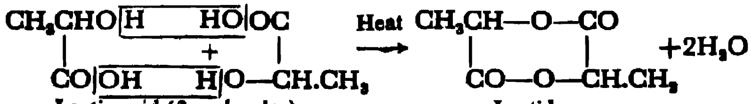
Chemical. Their molecules are made up of (*i*) one or more hydroxyl groups, and (*ii*) one or more carboxyl groups. Their properties are, therefore, properties of these groups as given under individual acids.

Action of heat on various hydroxy acids is of special interest and the products obtained are determined by the relative positions of the two functional groups as illustrated below :

(*i*) **α-hydroxy acids** give rise to cylic anhydrides or lactides by the elimination of two molecules of water from two molecules of the acids when —OH group of one reacts with the —COOH group of the other and *vice versa.*

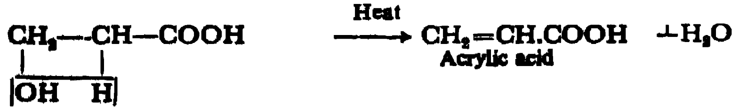


Glycollic acid (*2 molecules*) Lactide (*glycollide*)

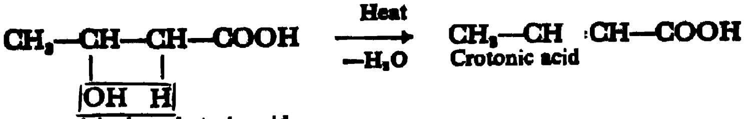


Lactic acid (*2 molecules*) Lactide

(*ii*) **β-hydroxy acids** lose a molecule of water on heating, producing an unsaturated acid.



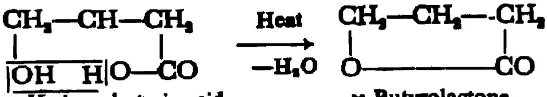
β-hydroxypropionic acid



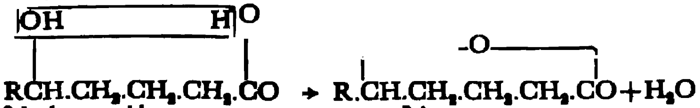
$$CH_3-\underset{OH}{CH}-\underset{H}{CH}-COOH \xrightarrow[-H_2O]{Heat} CH_3-CH{:}CH-COOH$$

β-hydroxybutyric acid Crotonic acid

(*iii*) **γ- and δ-hydroxy acids** are very interesting in this respect and lose a molecule of water more readily by the interaction of the —OH and —COOH groups of the same molecule. On heating an aqueous solution of a γ- or δ-hydroxy acid, it loses water to produce inner ester known as lactone.



γ-Hydroxybutyric acid γ-Butyrolactone



δ-hydroxy acid δ-lactone

α-, β-, and γ-hydroxy acids can be distinguished from one another by their behaviour on heating.

SOME INDIVIDUAL MEMBERS

4. **Glycollic acid, Hydroxyacetic acid, Hydroxyethanoic acid, $CH_2(OH).COOH$.**—It is the simplest hydroxyacid found in unripe grapes, tomatoes and sugar-cane juice.

Preparation. (*i*) *By refluxing an aqueous solution of potassium chloroacetate with sodium carbonate and then acidifying the mixture with hydrochloric acid.*

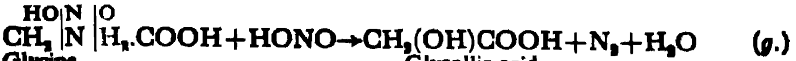
$$CH_2Cl.COOK+H_2O \rightarrow CH_2OH.COOH+KCl \qquad (80\%)$$

(*ii*) *By warming formalin with potassium cyanide solution and then acidifying the product with hydrochloric acid.*

$$HCHO + KCN + 2H_2O \xrightarrow{-NH_3} CH_2OH.COOK$$

$$\xrightarrow{HCl} CH_2OH.COOH \ (70\%)$$

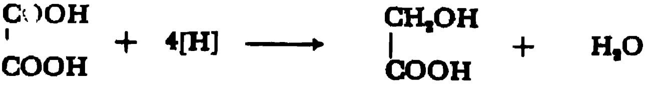
(*iii*) *By the action of nitrous acid on glycine.*



$$CH_2\,NH_2.COOH+HONO \rightarrow CH_2(OH)COOH+N_2+H_2O \qquad (g.)$$

Glycine Glycollic acid

(*iv*) *Manufacture.* Glycollic acid is prepared industrially by the electrolytic reduction of oxalic acid.



$$\begin{matrix}COOH\\|\\COOH\end{matrix} + 4[H] \longrightarrow \begin{matrix}CH_2OH\\|\\COOH\end{matrix} + H_2O$$

A more recent method for the same is by heating (at 433-443K) under pressure a mixture of formalin, carbon monoxide and water in acetic acid with sulphuric acid as *catalyst.*

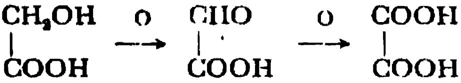
$$\underset{Formalin}{HCHO} + CO + H_2O \rightarrow \underset{Glycollic\ acid}{CH_2OH.COOH}$$

Properties : Physical. Glycollic acid is a hygroscopic, crystalline solid (m.p. 353K), readily soluble in water, ethanol and ether.

Chemical. The molecule of glycollic acid is made up of (*i*) one primary alcoholic group (—CH_2OH), and (*ii*) one carboxyl group (—COOH). Its properties are, therefore, the properties of these two groups as given below :

1. *Reactions of the Alcoholic Group* :

(*i*) **Oxidation**. Upon oxidation, it gives glyoxalic acid and then oxalic acid.



$$\begin{array}{c}CH_2OH\\|\\COOH\end{array}\xrightarrow{O}\begin{array}{c}CHO\\|\\COOH\end{array}\xrightarrow{O}\begin{array}{c}COOH\\|\\COOH\end{array}$$

Glycollic acid — Glyoxalic acid — Oxalic acid

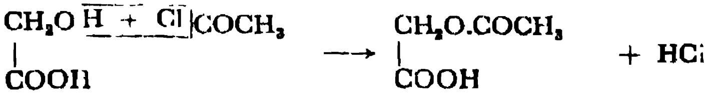
(*ii*) **With Halogen acids**. With hydrochloric acid, the —OH group is replaced by the Cl-atom while with hydriodic acid it is reduced to acetic acid.

$$CH_2(OH)COOH + HCl \longrightarrow CH_2Cl.COOH + H_2O$$

Glycollic acid — Monochloroacetic acid

$$CH_2(OH)COOH + 2HI \longrightarrow CH_3COOH + I_2 + H_2O$$

(*iii*) **Acetylation**. With acetyl chloride, the —OH group is acetylated.



$$\begin{array}{c}CH_2O\underline{H + Cl}|COCH_3\\|\\COOH\end{array}\longrightarrow\begin{array}{c}CH_2O.COCH_3\\|\\COOH\end{array}+HCl$$

2. *Reactions of the Carboxyl Group* :

(*i*) **With alkalis or carbonates**. Salts are produced by neutralization when glycollic acid reacts with alkalis or carbonates.

$$CH_2OH.COO|\underline{H + HO}|Na \longrightarrow CH_2OH.COONa + H_2O$$

Sod. glycollate

$$CH_2OH.COOH + NH_3 \longrightarrow CH_2OH.COONH_4$$

Amm. glycollate

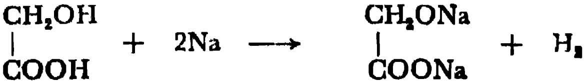
(*ii*) **Esterification**. With alcohols, glycollic acid gives esters.

$$CH_2OH.CO|\overline{OH + H}|OC_2H_5 \longrightarrow CH_2OH.COOC_2H_5 + H_2O$$

Glycollic acid — Ethyl alcohol — Ethyl glycollate

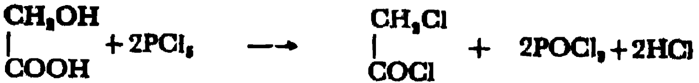
3. *Reactions involving both Groups* :

(*i*) **With metallic sodium**. Disodium glycollate is formed when glycollic acid reacts with metallic sodium.



$$\begin{array}{c}CH_2OH\\|\\COOH\end{array}+2Na\longrightarrow\begin{array}{c}CH_2ONa\\|\\COONa\end{array}+H_2$$

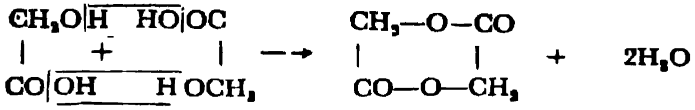
(*ii*) **With Phosphorus pentachloride**. Glycollic acid reacts with phosphorus pentachloride when the two —OH groups are replaced by —Cl atoms to form chloroacetyl chloride.



$$\begin{array}{l}CH_2OH\\ |\\ COOH\end{array} + 2PCl_5 \longrightarrow \begin{array}{l}CH_2Cl\\ |\\ COCl\end{array} + 2POCl_3 + 2HCl$$

Glycollic acid   Chloroacetyl chloride

(*iii*) **Action of Heat.** On heating two molecules of glycollic acid form a *glycollide* by elimination of two molecules of water.



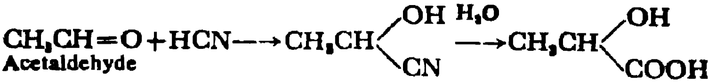
$$\begin{array}{l}CH_2O|H\quad HO|OC\\ |\qquad\quad + \qquad\quad |\\ CO|OH\quad\; H|OCH_2\end{array} \longrightarrow \begin{array}{l}CH_2-O-CO\\ |\qquad\qquad\quad |\\ CO-O-CH_2\end{array} + 2H_2O$$

Glycollide

Uses. Glycollic acid is largely used in cloth-printing.

5. Lactic acid (*α-hydroxypropionic acid, 2-hydroxypropanoic acid*), $CH_3CHOH.COOH$.—Lactic acid is present in milk whence it derives its name (Latin *lac*=milk).

Preparation. Lactic acid may be prepared : (*i*) *By the hydrolysis of the cyanohydrin of acetaldehyde.*



$$CH_3CH{=}O + HCN \longrightarrow CH_3CH\begin{array}{l}\diagup OH\\ \diagdown CN\end{array} \xrightarrow{H_2O} CH_3CH\begin{array}{l}\diagup OH\\ \diagdown COOH\end{array}$$

Acetaldehyde   Cyanohydrin   Lactic acid

(*ii*) *By the hydrolysis of α-bromopropionic acid* with silver oxide in water or with sodium hydroxide solution.

$$CH_3.CHBr.COOH + HOH \rightarrow CH_3CH(OH)COOH + HBr \quad (g.\text{-}v.g.)$$

(*iii*) **Manufacture.** Technically lactic acid is prepared by the fermentation of sugar with lactic bacilli (in sour milk or decaying cheese) at 310-315K in the presence of powdered chalk. Chalk helps to keep the acidity below 1% and is necessary because even 1% free acid renders the bacilli inactive. Crystals of calcium lactate separate and are removed. Free acid is regenerated from the calcium salt with requisite quantity of dilute sulphuric acid. The calcium sulphate is filtered off and the filtrate distilled under reduced pressure to get free lactic acid.

Properties : Physical. Lactic acid is a colourless syrupy liquid (m.p. 291K ; b.p. 395K) having a sour taste and smell. It is hygroscopic in nature and is very soluble in water. It is optically active and exists in three distinct forms (*see* page 1·190).

Chemical. Lactic acid resembles glycollic acid and gives the usual reactions of an alcoholic (OH) and a carboxyl (COOH) group. For example, it gives salts with alkalis, esters with alcohols and acid chloride with phosphorus pentachloride. With halogen acids also it gives the usual reactions of an alcoholic group A few special reactions are :

(*i*) **Oxidation.** On oxidation with hydrogen peroxide, lactic acid gives pyruvic acid—a ketonic acid (showing the presence of a secondary alcoholic group).

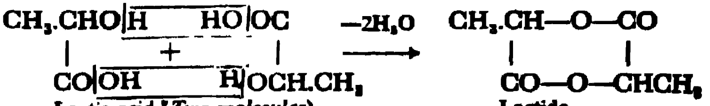
$$CH_3.CH(OH).COOH \xrightarrow{O} CH_3CO.COOH + H_2O$$

Lactic acid   Pyruvic acid

Oxidation with dilute acidified potassium permanganate, however, yields acetaldehyde.

$$CH_3CH(OH).COOH+O \xrightarrow{KMnO_4} CH_3CHO+CO_2+H_2O$$

(*ii*) **Heat.** When heated, a lactide is formed (*cf.*, glycollide).



$$\begin{array}{l} CH_3.CHO|H \quad HO|OC \\ \quad | \qquad + \qquad | \\ \quad CO|OH \quad H|OCH.CH_3 \end{array} \xrightarrow{-2H_2O} \begin{array}{l} CH_3.CH—O—CO \\ \quad | \qquad\qquad | \\ \quad CO—O—CHCH_3 \end{array}$$

Lactic acid (*Two molecules*) Lactide

(*iii*) **Hydrolysis.** When heated with dilute sulphuric acid, lactic acid undergoes hydrolysis as given below :

$$\underset{\text{Lactic acid}}{CH_3.CH(OH)COOH} \rightarrow \underset{\text{Acetaldehyde}}{CH_3CHO} + \underset{\text{Formic acid}}{HCOOH}$$

Concentrated sulphuric acid brings about the hydrolysis more rapidly and decomposes formic acid further into carbon monoxide and water.

Uses. (*i*) For removing lime from hides.

(*ii*) In dyeing industry.

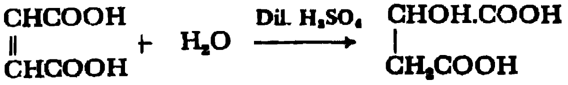
(*iii*) Ethyl lactate finds use as a solvent for cellulose nitrate.

(*iv*) Calcium lactate is used in medicine and in baking powder.

6. Malic Acid, Monohydroxysuccinic acid, HOOC.CH$_2$.CHOH.COOH.—Malic acid occurs in sour apples, grapes and berries. Scheele prepared it first in 1785 from unripe apples (Latin, *malum*—apple) and hence the name.

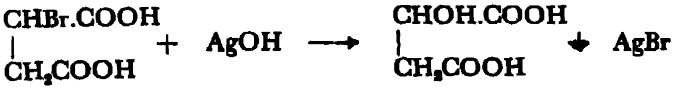
Preparation. (*i*) *Malic acid may be prepared from mountainous berries.* The juice is boiled with calcium hydroxide solution when calcium malate is precipitated. The precipitate is filtered and decomposed with a calculated quantity of dilute sulphuric acid.

(*ii*) *By heating maleic acid with dilute sulphuric acid under pressure.*



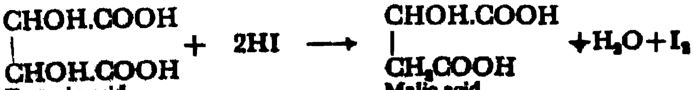
$$\begin{array}{l} CHCOOH \\ \| \\ CHCOOH \end{array} + H_2O \xrightarrow{\text{Dil. } H_2SO_4} \begin{array}{l} CHOH.COOH \\ | \\ CH_2COOH \end{array}$$

(*iii*) In the laboratory it can be conveniently prepared *by heating bromosuccinic acid with silver oxide suspended in water.*



$$\begin{array}{l} CHBr.COOH \\ | \\ CH_2COOH \end{array} + AgOH \longrightarrow \begin{array}{l} CHOH.COOH \\ | \\ CH_2COOH \end{array} + AgBr$$

(*iv*) *By careful reduction of tartaric acid with concentrated hydriodic acid.*



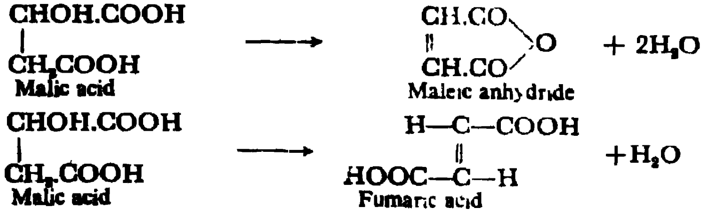
$$\begin{array}{l} CHOH.COOH \\ | \\ CHOH.COOH \end{array} + 2HI \longrightarrow \begin{array}{l} CHOH.COOH \\ | \\ CH_2COOH \end{array} + H_2O + I_2$$

Tartaric acid Malic acid

Properties : Physical. Malic acid is a colourless, crystalline and deliquescent solid readily soluble in water and alcohol. It is optically active and exists in three distinct forms (*see* page 1·192).

Chemical. It behaves both as a secondary alcohol and a dibasic acid. Inspection of the formula shows it to be an α-hydroxyacid with respect to one carboxyl group and a β-hydroxyacid with respect to the other :

(*i*) On heating, it eliminates water to form maleic anhydride and fumaric acid—an unsaturated acid (not a lactide). Thus it behaves like a β-hydroxyacid.



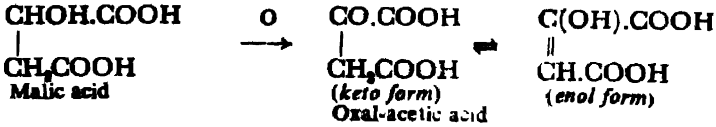
$$\underset{\text{Malic acid}}{\begin{array}{l}\text{CHOH.COOH}\\ |\\ \text{CH}_2\text{COOH}\end{array}} \longrightarrow \underset{\text{Maleic anhydride}}{\begin{array}{l}\text{CH.CO}\diagdown\\ \|\qquad\quad >\text{O}\\ \text{CH.CO}\diagup\end{array}} + 2\text{H}_2\text{O}$$

$$\underset{\text{Malic acid}}{\begin{array}{l}\text{CHOH.COOH}\\ |\\ \text{CH}_2\text{COOH}\end{array}} \longrightarrow \underset{\text{Fumaric acid}}{\begin{array}{c}\text{H—C—COOH}\\ \|\\ \text{HOOC—C—H}\end{array}} + \text{H}_2\text{O}$$

(*ii*) On reduction with hydriodic acid, it yields succinic acid

$$\begin{array}{l}\text{CHOH.COOH}\\ |\\ \text{CH}_2\text{COOH}\end{array} + 2\text{HI} \longrightarrow \begin{array}{l}\text{CH}_2\text{.COOH}\\ |\\ \text{CH}_2\text{.COOH}\end{array} + \text{I}_2 + \text{H}_2\text{O}$$

(*iii*) On careful oxidation, it is converted into oxal-acetic acid—an acid which exhibits keto-enol tautomerism like acetoacetic acid.

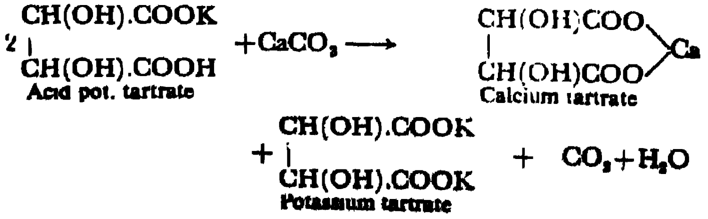


$$\underset{\text{Malic acid}}{\begin{array}{l}\text{CHOH.COOH}\\ |\\ \text{CH}_2\text{COOH}\end{array}} \xrightarrow{\text{O}} \underset{\substack{(\textit{keto form})\\ \text{Oxal-acetic acid}}}{\begin{array}{l}\text{CO.COOH}\\ |\\ \text{CH}_2\text{COOH}\end{array}} \rightleftharpoons \underset{(\textit{enol form})}{\begin{array}{l}\text{C(OH).COOH}\\ \|\\ \text{CH.COOH}\end{array}}$$

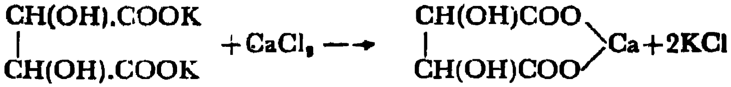
Uses. Malic acid is gradually replacing citric and tartaric acids used in beverages. It is also used as a purgative and as a remedy for sore-throat.

7. **Tartaric acid** (*α : α′-dihydroxysuccinic acid*), **HOOC.CHOH.CHOH.COOH.**—

Manufacture. Tartaric acid as such or as its potassium salt occurs in grapes, tamarind (इमली) and berries. *Argol* which separates as crust during the fermentation of grape juice is impure acid potassium tartrate. It is boiled with chalk until neutral. Calcium tartrate precipitate is filtered and potassium tartrate in the filtrate is also precipitated with calcium chloride.

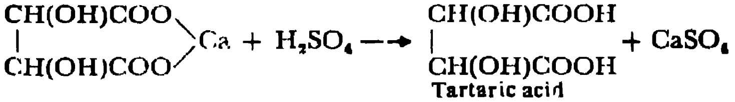


$$2\underset{\text{Acid pot. tartrate}}{\begin{array}{l}\text{CH(OH).COOK}\\ |\\ \text{CH(OH).COOH}\end{array}} + \text{CaCO}_3 \longrightarrow \underset{\text{Calcium tartrate}}{\begin{array}{l}\text{CH(OH)COO}\diagdown\\ |\qquad\qquad\quad\ \ \text{Ca}\\ \text{CH(OH)COO}\diagup\end{array}} + \underset{\text{Potassium tartrate}}{\begin{array}{l}\text{CH(OH).COOK}\\ |\\ \text{CH(OH).COOK}\end{array}} + \text{CO}_2 + \text{H}_2\text{O}$$



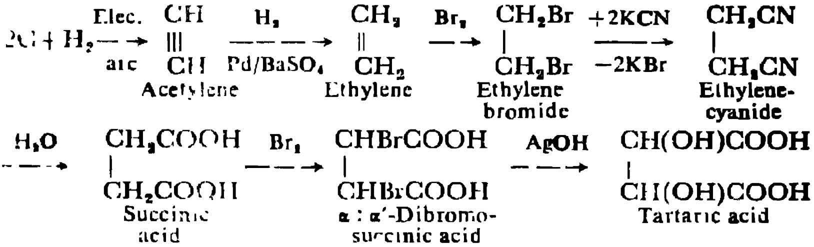
$$\begin{array}{l}\text{CH(OH).COOK}\\ |\\ \text{CH(OH).COOK}\end{array} + CaCl_2 \longrightarrow \begin{array}{l}\text{CH(OH)COO}\\ |\\ \text{CH(OH)COO}\end{array}\!\!\!>\!Ca + 2KCl$$

The precipitate of calcium tartrate is decomposed with dilute sulphuric acid (calculated quantity) and filtered when calcium sulphate is left as residue and tartaric acid crystals are separated on concentrating the filtrate.



$$\begin{array}{l}\text{CH(OH)COO}\\ |\\ \text{CH(OH)COO}\end{array}\!\!\!>\!Ca + H_2SO_4 \longrightarrow \underset{\text{Tartaric acid}}{\begin{array}{l}\text{CH(OH)COOH}\\ |\\ \text{CH(OH)COOH}\end{array}} + CaSO_4$$

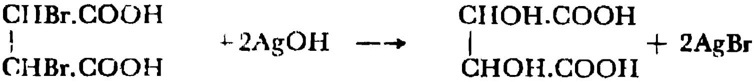
Synthesis (*i*) Tartaric acid can be synthesised from elements as follows :



$$2C + H_2 \xrightarrow[\text{arc}]{\text{Elec.}} \underset{\text{Acetylene}}{\begin{array}{l}CH\\ |||\\ CH\end{array}} \xrightarrow[Pd/BaSO_4]{H_2} \underset{\text{Ethylene}}{\begin{array}{l}CH_2\\ ||\\ CH_2\end{array}} \xrightarrow{Br_2} \underset{\text{Ethylene bromide}}{\begin{array}{l}CH_2Br\\ |\\ CH_2Br\end{array}} \xrightarrow[-2KBr]{+2KCN} \underset{\text{Ethylene-cyanide}}{\begin{array}{l}CH_2CN\\ |\\ CH_2CN\end{array}}$$

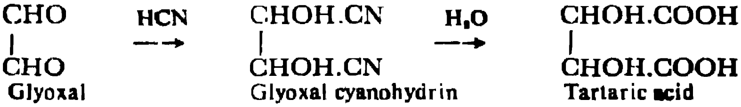
$$\xrightarrow{H_2O} \underset{\text{Succinic acid}}{\begin{array}{l}CH_2COOH\\ |\\ CH_2COOH\end{array}} \xrightarrow{Br_2} \underset{\alpha : \alpha'\text{-Dibromosuccinic acid}}{\begin{array}{l}CHBrCOOH\\ |\\ CHBrCOOH\end{array}} \xrightarrow{AgOH} \underset{\text{Tartaric acid}}{\begin{array}{l}CH(OH)COOH\\ |\\ CH(OH)COOH\end{array}}$$

(*ii*) It can also be synthesised by boiling α : α′-dibromosuccinic acid with silver oxide suspended in water.



$$\begin{array}{l}\text{CHBr.COOH}\\ |\\ \text{CHBr.COOH}\end{array} + 2AgOH \longrightarrow \begin{array}{l}\text{CHOH.COOH}\\ |\\ \text{CHOH.COOH}\end{array} + 2AgBr$$

(*iii*) The acid is also formed by the hydrolysis of glyoxal cyanohydrin.

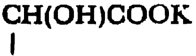


$$\underset{\text{Glyoxal}}{\begin{array}{l}CHO\\ |\\ CHO\end{array}} \xrightarrow{HCN} \underset{\text{Glyoxal cyanohydrin}}{\begin{array}{l}\text{CHOH.CN}\\ |\\ \text{CHOH.CN}\end{array}} \xrightarrow{H_2O} \underset{\text{Tartaric acid}}{\begin{array}{l}\text{CHOH.COOH}\\ |\\ \text{CHOH.COOH}\end{array}}$$

Properties : Physical. It is a colourless crystalline substance (m.p. 440K) soluble in water and alcohol but insoluble in ether. It is optically active and due to the presence of two asymmetric carbon atoms, occurs in four isomeric forms (*optical isomerides—see* page 1·193).

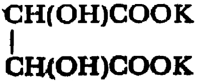
Chemical. A molecule of tartaric acid is made of (*i*) two secondary alcoholic groups, >CHOH, (*ii*) two carboxyl groups —COOH. Its properties are, therefore, the properties of these groups. For example,

(*i*) It gives two series of salts, when treated with alkalis or carbonates.



$$\begin{array}{l}\text{CH(OH)COOK}\\ |\\ \text{CH(OH)COOH}\end{array}$$

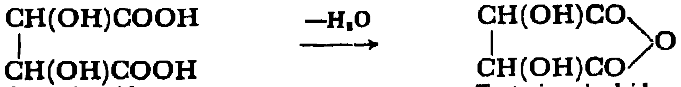
Acid pot. tartrate



$$\begin{array}{l}\text{CH(OH)COOK}\\ |\\ \text{CH(OH)COOK}\end{array}$$

normal pot. tartrate

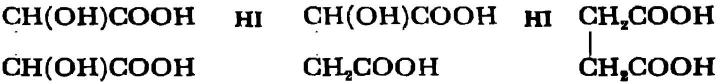
(*ii*) It gives the anhydride on prolonged heating (425K) but chars at higher temperatures.



$$\begin{array}{l}\text{CH(OH)COOH}\\ |\\ \text{CH(OH)COOH}\end{array} \xrightarrow{-H_2O} \begin{array}{l}\text{CH(OH)CO}\\ |\\ \text{CH(OH)CO}\end{array}\!\!>\!O$$

Tartaric acid **Tartaric anhydride**

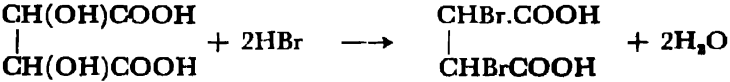
(*iii*) With hydriodic acid, the two —OH groups are successively replaced by H-atoms and we get first malic acid and then succinic acid.



$$\begin{array}{l}\text{CH(OH)COOH}\\ \\ \text{CH(OH)COOH}\end{array} \xrightarrow{\text{HI}} \begin{array}{l}\text{CH(OH)COOH}\\ \\ CH_2COOH\end{array} \xrightarrow{\text{HI}} \begin{array}{l}CH_2COOH\\ |\\ CH_2COOH\end{array}$$

Tartaric acid **Malic acid** **Succinic acid**

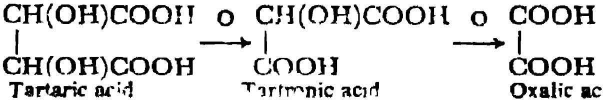
(*iv*) With hydrobromic acid, the two —OH groups are replaced by two Br-atoms to give dibromosuccinic acid.



$$\begin{array}{l}\text{CH(OH)COOH}\\ |\\ \text{CH(OH)COOH}\end{array} + 2HBr \longrightarrow \begin{array}{l}\text{CHBr.COOH}\\ |\\ \text{CHBrCOOH}\end{array} + 2H_2O$$

Dibromosuccinic acid

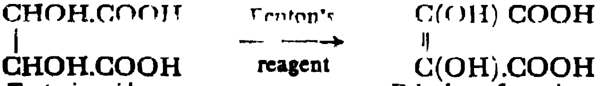
(*v*) Oxidation of tartaric acid gives tartronic acid but with strong oxidising agents, oxalic acid is produced.



$$\begin{array}{l}\text{CH(OH)COOH}\\ |\\ \text{CH(OH)COOH}\end{array} \xrightarrow{O} \begin{array}{l}\text{CH(OH)COOH}\\ |\\ \text{COOH}\end{array} \xrightarrow{O} \begin{array}{l}\text{COOH}\\ |\\ \text{COOH}\end{array}$$

Tartaric acid Tartronic acid Oxalic acid

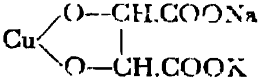
With Fenton's reagent (H_2O_2+ a ferrous salt), tartaric acid is oxidised to dihydroxy fumaric acid.



$$\begin{array}{l}\text{CHOH.COOH}\\ |\\ \text{CHOH.COOH}\end{array} \xrightarrow[\text{reagent}]{\text{Fenton's}} \begin{array}{l}\text{C(OH) COOH}\\ \|\\ \text{C(OH).COOH}\end{array}$$

Tartaric acid Dihydroxyfumaric acid

(*vi*) *Formation of complexes.* In Fehling's solution ($CuSO_4$+ Rochelle salt+NaOH) the insoluble copper hydroxide first formed goes in solution due to the formation of a complex. The structure of complex is uncertain. It may be



$$Cu\begin{array}{l}\diagup O\text{—CH.COONa}\\ \qquad\quad |\\ \diagdown O\text{—CH.COOK}\end{array}$$

Uses. (*i*) In effervescent drinks and in making saline drinks.

(*ii*) ***Rochelle salt*** (Sodium potassium tartrate) is used in Fehling's solution, Seidlitz powder (a laxative) and in silvering of mirrors.

(*iii*) ***Tartar emetic*** potassium antimonyl tartrate, $[C_4H_4O_6K(SbO).\frac{1}{2}H_2O]$ is used in medicine as emetic and in dyeing and calico-printing as mordant.

(*iv*) ***Cream of tartar*** (potassium acid tartrate) is used in dyeing and making baking powders.

Tests. (*i*) **When heated strongly, tartaric acid or tartrates char rapidly giving a smell of burnt sugar.**

(*ii*) With hot concentrated sulphuric acid charring and smell of burnt sugar is accompanied by the evolution of carbon monoxide, carbon dioxide and sulphur dioxide.

(*iii*) A neutral solution of a tartrate gives with silver nitrate a white precipitate soluble in ammonia. A silver mirror is obtained on warming the ammoniacal solution.

(*iv*) With calcium chloride, the neutral solution of a tartrate gives a white precipitate soluble in sodium hydroxide. The precipitate reappears on boiling the solution (*Distinction from oxalates*).

(*v*) On adding Fenton's reagent (hydrogen peroxide containing a little of ferrous salt) and caustic soda, tartrates give a violet coloration.

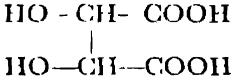
Structure. (*i*) The molecular formula of tartaric acid as determined from its analytical data and molecular weight determination is $C_4H_6O_6$.

(*ii*) It gives two series of salts and esters. This shows the presence of two —COOH groups.

(*iii*) Since it does not give any carbon dioxide on heating, the two carboxyl groups must be attached to two different carbon atoms.

(*iv*) Its ethyl ester gives a diacetyl derivative with acetic anhydride. This shows the presence of two —OH groups in the molecule. The two —OH groups must be attached to two different carbon atoms as the molecule is quite stable.

(*v*) Keeping all these facts in view, the only possible structural formula for tartaric acid could be



$$\begin{array}{c}HO-CH-COOH\\ |\\ HO-CH-COOH\end{array}$$

(*vi*) This is further confirmed by the fact that it gives succinic acid on reduction with hydriodic acid. It is also supported by its synthesis from glyoxal as given above.

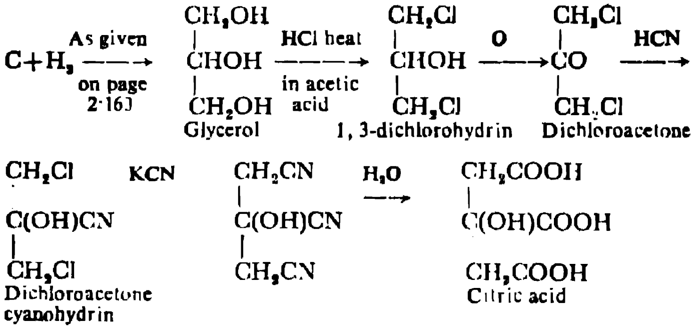
8. **Citric acid** (*2-hydroxypropane-1 : 2 : 3-tricarboxylic acid*), **$HOOC.CH_2—C(OH).COOH—CH_2.COOH$.**—Citrus fruits such as lemon, lime, orange and *galgal* which contain free citric acid constitute the *natural sources* of the acid, *e.g.*, lemon juice contains 6-10 per cent of citric acid.

Preparation. Different methods used for the industrial preparation of citric acid are :

(*i*) **From citrus fruits.** Juice of any of the citrus fruits given above is extracted and boiled. The albuminous matter is coagulated and filtered off. The filtrate is neutralized with chalk ($CaCO_3$) and filtered again. Calcium citrate is deposited when the filtrate is boiled. This is separated and decomposed with a calculated amount of sulphuric acid. Calcium sulphate precipitate is removed and the solution concentrated to get citric acid crystals.

(*ii*) **From Sugar or Molasses.** The acid is now being manufactured by fermentation of dilute sugar solution or diluted molasses, in the presence of certain inorganic salts by various moulds or fungi, *e.g.*, *Citromyces prefferianus*.

Synthesis. Citric acid may be synthesised from elements by the following reactions, this synthesis also shows its structure.



$$C+H_2 \xrightarrow[\text{on page 2·163}]{\text{As given}} \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} \xrightarrow[\text{in acetic acid}]{\text{HCl heat}} \begin{array}{l} CH_2Cl \\ | \\ CHOH \\ | \\ CH_2Cl \end{array} \xrightarrow{O} \begin{array}{l} CH_2Cl \\ | \\ CO \\ | \\ CH_2Cl \end{array} \xrightarrow{HCN}$$

Glycerol 1, 3-dichlorohydrin Dichloroacetone

$$\begin{array}{l} CH_2Cl \\ | \\ C(OH)CN \\ | \\ CH_2Cl \end{array} \xrightarrow{KCN} \begin{array}{l} CH_2CN \\ | \\ C(OH)CN \\ | \\ CH_2CN \end{array} \xrightarrow{H_2O} \begin{array}{l} CH_2COOH \\ | \\ C(OH)COOH \\ | \\ CH_2COOH \end{array}$$

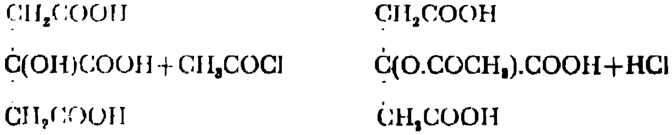
Dichloroacetone cyanohydrin Citric acid

Properties : Physical. Citric acid crystallizes as white monohydrate crystals which lose the water of crystallization at 403K and melt at 426K. It is readily soluble in water and alcohol but insoluble in ether. It is not optically active.

Chemical. It behaves both as an alcohol and tribasic acid *e.g.*,

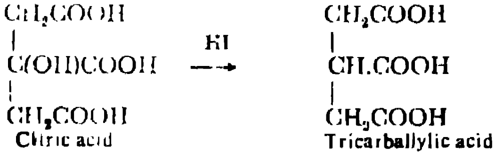
(*i*) With alkalis or alcohols it gives three series of salts and esters.

(*ii*) With acetyl chloride, it forms the monoacetyl derivative.



$$\begin{array}{l} CH_2COOH \\ | \\ C(OH)COOH \\ | \\ CH_2COOH \end{array} + CH_3COCl \longrightarrow \begin{array}{l} CH_2COOH \\ | \\ C(O.COCH_3).COOH \\ | \\ CH_2COOH \end{array} + HCl$$

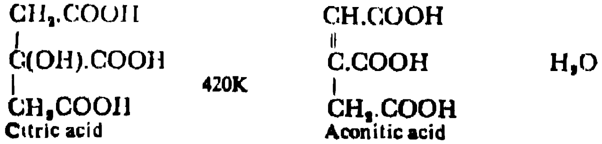
(*iii*) On reduction with hydriodic acid, citric acid gives tricarballylic acid.



$$\begin{array}{l} CH_2COOH \\ | \\ C(OH)COOH \\ | \\ CH_2COOH \end{array} \xrightarrow{HI} \begin{array}{l} CH_2COOH \\ | \\ CH.COOH \\ | \\ CH_2COOH \end{array}$$

Citric acid Tricarballylic acid

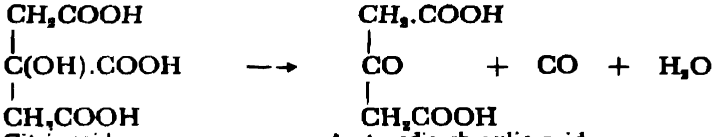
(*iv*) On heating to 423K, it loses a molecule of water to give *aconitic acid*.



$$\begin{array}{l} CH_2.COOH \\ | \\ C(OH).COOH \\ | \\ CH_2COOH \end{array} \xrightarrow{420K} \begin{array}{l} CH.COOH \\ \| \\ C.COOH \\ | \\ CH_2.COOH \end{array} \quad H_2O$$

Citric acid Aconitic acid

(*v*) On heating with concentrated sulphuric acid, aconitic acid is obtained but with fuming sulphuric acid, citric acid forms acetonedicarboxylic acid.



$$\begin{array}{l} CH_2COOH \\ | \\ C(OH).COOH \\ | \\ CH_2COOH \end{array} \longrightarrow \begin{array}{l} CH_2.COOH \\ | \\ CO \\ | \\ CH_2COOH \end{array} + CO + H_2O$$

Citric acid Acetonedicarboxylic acid

Uses. Citric acid finds use :

(*i*) In making beverages, *e.g.*, lemonades.

(*ii*) As a mordant in dyeing and calico-printing.

(*iii*) Ferric ammonium citrate, magnesium citrate, sodium or potassium citrate are used in medicine.

(*iv*) Ferric ammonium citrate also finds use in making blue-prints.

(*v*) Esters of citric acid (*e.g.*, tributyl citrate) find use as plasticizers for lacquers and varnishes.

Tests. (*i*) When heated gently with concentrated sulphuric acid, carbon monoxide is evolved and the mass turns dark brown. When heated alone, citric acid chars giving irritating vapours but no smell of burnt sugar (*cf.* tartaric acid).

(*ii*) No precipitate is obtained when calcium chloride is added to the neutral solution of a citrate. On boiling, however, a white precipitate is obtained which is insoluble in caustic soda but soluble in acetic acid.

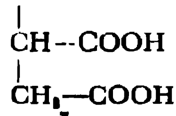
(*iii*) With ammoniacal silver nitrate, the neutral solution of a citrate gives a white precipitate soluble in ammonia. Silver is deposited slowly on boiling this solution.

Structure. (*i*) The molecular formula of citric acid as deduced from its analytical data and molecular weight determination is $C_6H_8O_7$.

(*ii*) It gives three series of salts and esters. This shows it is a tribasic acid. It does not give any carbon dioxide on heating. The three carboxyl groups must, therefore, be attached with three different carbon atoms.

(*iii*) With acetic anhydride, citric acid gives a monoacetyl derivative. This shows the presence of one —OH group.

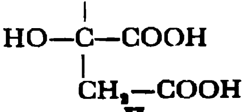
(*iv*) Keeping these facts in view, the possible structures of citric acid are :



$$\begin{array}{l} HO—CH—COOH \\ \quad\quad\ | \\ \quad\quad CH—COOH \\ \quad\quad\ | \\ \quad\quad CH_2—COOH \end{array}$$

I

or



$$\begin{array}{l} \quad\quad CH_2COOH \\ \quad\quad\ | \\ HO—C—COOH \\ \quad\quad\ | \\ \quad\quad CH_2—COOH \end{array}$$

II

(*v*) Synthesis of the acid as given above supports the formula II. Hence formula II represents the structure of citric acid.

QUESTIONS

Essay Type :

1. Enumerate the general methods for the preparation of aliphatic hydroxyacids and explain how will you proceed to distinguish α-, β- and γ-hydroxyacids from one another ? (*Jammu B.Sc. 1977* ; *Kashmir 1975* ; *Delhi 1971*)

2. *How is glycollic acid prepared ? What are its properties ?*

3. Describe the method of preparation of lactic acid. How does it react with (*i*) Hydrogen peroxide. (*ii*) Hot dilute sulphuric acid. (*iii*) Dilute acidified potassium permanganate ? What happens when it is heated ? How many optical isomers of lactic acid are known ? Give their structures.
(*Delhi Pre-Med. 1972*)

4. Give two methods for the synthesis of lactic acid. Describe the properties of the acid and discuss its isomerism. (*Calicut B.Sc. 1973*)

5. (*a*) How are the different forms of tartaric acid prepared ? What are their important properties ? How is their isomerism explained ?
(*Calicut B.Sc. 1972* ; *Meerut B.Sc. 1968*; *Rajasthan 1968*)

6. How is citric acid prepared ? Describe its important properties and discuss its structure. How does it differ from tartaric acid ?
(*Kerala B Sc. 1972* ; *Delhi 1971*)

7. What are α-, β- and γ-hydroxyacids and how are these differentiated ? Establish the structure of citric acid by rational synthesis. How does citric acid react with acetyl chloride and hydriodic acid ? (*Delhi B.Sc. 1971* ; *Punjab 1969*)

8. Starting from $CH_2BrCOOC_2H_5$ how will you synthesise citric acid ? Give tests to distinguish citric acid from tartaric acid. What happens when citric acid is—(*i*) heated to 423K, (*ii*) heated with fuming H_2SO_4, and (*iii*) subjected to pyrolysis ? (*Rajasthan B Sc. 1970*)

Short Answer Type :

1. How would you show that lactic acid is an β-hydroxy acid ?
(*Delhi B.Sc. 1976 Supp.*)

2. How would you synthesise tartaric acid, starting from acetylene ? Indicate the reagent and conditions employed for each step involved.
(*Delhi B.Sc. 1976*)

3. How will you synthesise tartaric acid from ethene ? Give one test for tartaric acid. (*Delhi B.Sc. 1976*)

4. What happens when tartaric acid is treated with (*a*) hydriodic acid, (*b*) conc. H_2SO_4, (*c*) hydrobromic acid, (*d*) PCl_5 ? (*Delhi B.Sc. 1977, 76*)

5. Describe the process of recovery of tartaric acid from fermentation of grape juice. (*Delhi B.Sc. 1976*)

6. How would you show that malic acid is—
(*i*) an α-hydroxy acid, (*ii*) a β-hydroxy acid.
(*Delhi B.Sc. 1976*)

7. Give the synthesis of citric acid. (*Jammu B.Sc. 1977*)

8. How is lactic acid prepared ? What happens when it is subjected to mild oxidation ? (*Delhi B.Sc. 1978 Supp.*)

9. Why are three varieties of lactic acids known ? How many of them are optically active ? Write their structures. (*Delhi B Sc. 1978 Supp.*)

10. How will you justify the presence of three carbonyl groups and one hydroxyl group in the molecule of citric acid ? (*Delhi B.Sc. 1978 Supp.*)

11. What happens when citric acid is subjected to : (*i*) heat, (*ii*) heating in presence of fuming sulphuric acid ? (*Delhi B.Sc. 1978 Supp.*)

12. How is citric acid obtained from 1, 3-dichloro -2-propanone ?
(*Delhi B.Sc. 1978 Supp.*)

13. Starting from acetylene how can you get tartaric acid ?
(*Delhi B.Sc. Hons. Sub. 1978 Supp.*)

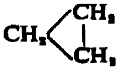
14. What is the effect of heat on α- and γ-hydroxy monocarboxylic acid ?
(*Delhi B.Sc. 1978*)

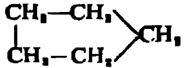
33

Alicyclic Compounds

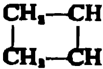
1. **Alicyclic Compounds.**—So far we have discussed the open chain compounds called aliphatic compounds and their derivatives. There are a large number of compounds having closed chains of carbon atoms. These are called carbocyclic or homocyclic compounds. A number of carbocyclic compounds resemble aliphatic compounds in many ways and are, therefore, called *alicyclic* compounds (from *aliphatic* and *cyclic* compounds).

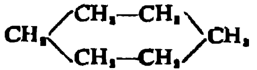
Saturated alicyclic hydrocarbons have the general formula C_nH_{2n} (same as that of the olefins) but they do not contain any double bond. Since they are made up of a number of methylene groups arranged in closed chains, they were named polymethylenes, *e.g.*,


Trimethylene

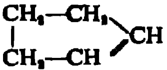

Pentamethylene

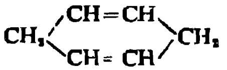
According to the IUPAC system, saturated alicyclic compounds are named as cycloalkanes or cycloparaffins. Individual members take the name of the corresponding alkane. For example,


Cyclobutane


Cyclohexane

Unsaturated alicyclic compounds are named after the corresponding aliphatic unsaturated compounds. Thus compounds with one double bond are cycloalkenes and others with two double bonds are cycloalkadienes. Some individual members are :

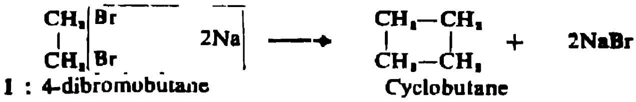

Cyclopentene


1,4-Cyclohexadiene

2. **Cycloalkanes, Cycloparaffins or Polymethylenes.**—Cycloalkanes are often termed naphthenes, as cycloalkanes containing five and six carbon atoms occur in naphtha, a fraction of petroleum. Three, four and five membered cycloalkanes occur in plants as essential oils (terpenes).

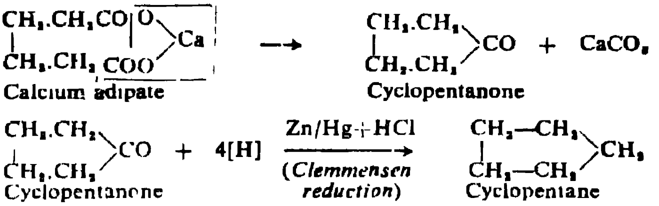
General Methods of Preparation

(*i*) *By treating α, ω-dihalogeno derivatives of alkanes with sodium or zinc, e.g.*, 1,4-dibromobutane forms cyclobutane.

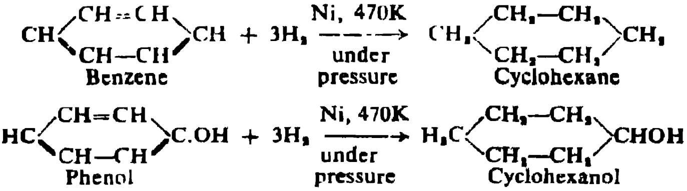


The method is an extension of Wurtz synthesis and may be regarded as internal Wurtz synthesis. Lower members up to cyclohexanes are prepared by this method.

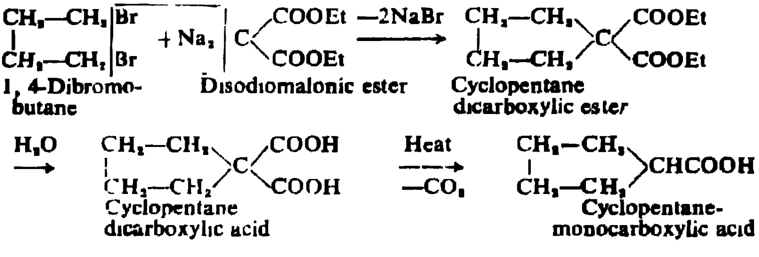
(*ii*) *By heating calcium or barium salt of a dicarboxylic acid and reduction of the cyclic ketone so obtained.*



(*iii*) Six-membered alicyclic compounds are conveniently prepared *by the catalytic reduction of benzene and its derivatives.*



(*iv*) *By treating alkylene halides with disodiomalonic ester followed by hydrolysis and heating.*


+ Na₂
—2NaBr
1, 4-Dibromobutane
Disodiomalonic ester
Cyclopentane dicarboxylic ester
H₂O
Cyclopentane dicarboxylic acid
Heat
—CO₂
Cyclopentane-monocarboxylic acid

General Properties : Physical. (*i*) First two members are colourless, pleasant smelling gases, next three members up to cycloheptane are liquids and higher ones are solids.

(*ii*) They are insoluble in water but soluble in ethanol and ether.

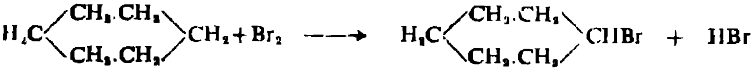
(*iii*) Their density and b.p. show a gradual increase with increase of molecular weight.

(*iv*) Their boiling points are higher than those of isomeric alkenes or corresponding alkanes as shown in table on the next page.

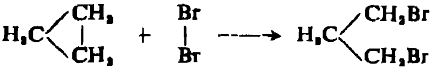
No. of Carbon atoms in the molecule	**Cycloalkane, C_nH_{2n}**		**Alkene, C_nH_{2n}**	**Alkane, C_nH_{2n+2}**
	Density of liquid	*b.p. K*	*b.p. K*	*b.p. K*
3	0·677	239·4	225	229·5
4	0·7038	258	268	273·6
5	0·7635	323	313	309·3
6	0·7934	354	337	342
7	0·8252	391	367·5	371·4
8	0·8502	420	393·5	399

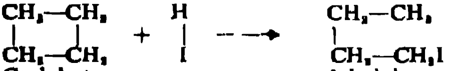
Chemical. Cycloalkanes have saturated molecules and give substitution reactions like alkanes. Cyclopropane and cyclobutane rings being under strain are comparatively less stable and tend to break open like a double bond. Thus in cycloalkanes are combined the properties of both alkanes and alkenes. For example,

(1) **Substitution reactions.** Cyclopentane and higher members give substitution products when treated with chlorine or bromine in diffused sunlight. For example,

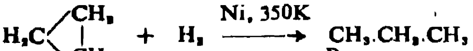

Cyclohexane Monobromocyclohexane

(2) **Addition reactions.** Cyclopropane and cyclobutane give addition products with halogen acids, sulphuric acid, etc.

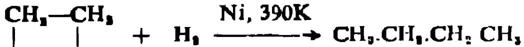

Cyclopropane 1, 3-Dibromopropane


Cyclobutane 1-Iodobutane

(3) **Catalytic reduction.** Lower members give alkanes when treated with hydrogen in presence of heated nickel.


Propane

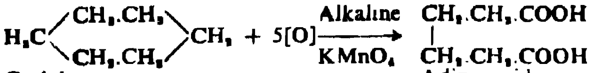
Cyclopropane


Butane

Cyclobutane

Similarly, cyclopentane is reduced to pentane when hydrogenated in the presence of nickel at 570K.

(4) **Oxidation.** Cycloalkanes are oxidised by alkaline potassium permanganate to give dicarboxylic acid with chain fission, *e.g.*,

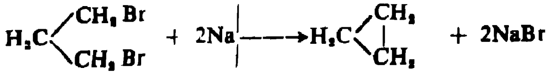

Cyclohexane Adipic acid

(5) **Relative Stability.** Stability of cycloalkanes increases with the size of the ring up to cyclopentane and higher members are quite stable. This has been explained at length under Baeyer's strain theory (*see* page). 2·40

INDIVIDUAL MEMBERS

3. Cyclopropane or Trimethylene, C_3H_6.—

Preparation. It is prepared by treating 1 : 3-dibromopropane in boiling xylene with metallic sodium.

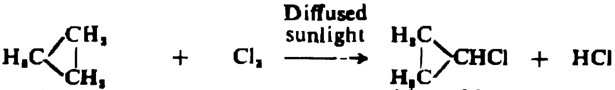


1 : 3-dibromopropane Cyclopropane

Properties. It is a colourless, pleasant smelling gas. It is slightly soluble in water but freely soluble in alcohol. It is a general anaesthetic. Oxygen mixed with 15-30% cyclopropane produces insensibility to pain and not unconsciousness but the disadvantage is that the mixture is explosive.

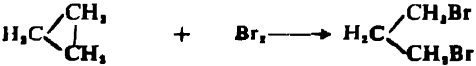
Its various chemical reactions are :

(*i*) With chlorine in the presence of diffused sunlight, it gives monosubstitution product.

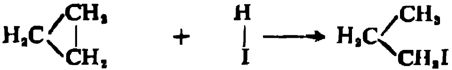


Cyclopropane Monochloro-cyclopropane

(*ii*) With bromine or hydriodic acid, the ring opens and an addition compound is obtained.

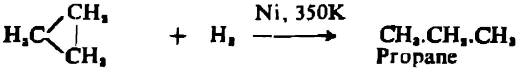


1 : 3-Dibromopropane

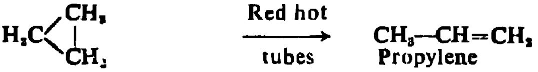


2-Iodopropane

(*iii*) On catalytic hydrogenation it gives propane while on passing through red hot tubes it forms propylene.



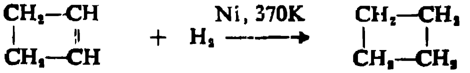
Propane



Propylene

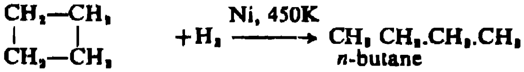
(*iv*) It does not decolorise potassium permanganate in the cold (*Distinction from isomeric propylene*).

4. Cyclobutane or Tetramethylene, C_4H_8.—It is usually prepared by reduction of cyclobutene with hydrogen in presence of nickel at 375K.

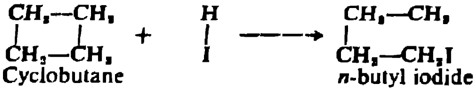


It is a colourless, pleasant-smelling gas (b.p. 258K). Chemically it is much more stable than cyclopropane, *e.g.*, it is unaffected by bromine, HI or $KMnO_4$ in the cold. Some of its chemical reactions are :

(*i*) On catalytic hydrogenation it gives *n*-butane.

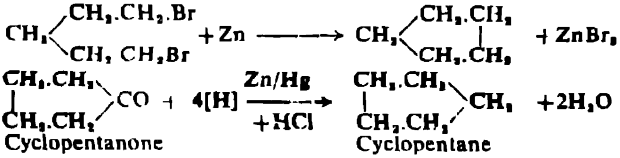


(*ii*) With HI it gives *n*-butyl iodide.



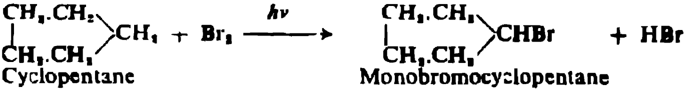
(*iii*) $KMnO_4$ has no action on cyclobutane.

5. **Cyclopentane or Pentamethylene, C_5H_{10}.**—It occurs in petroleum. It can be prepared by heating 1 : 5 dibromopentane with zinc or by the Clemmensen reduction of cyclopentanone.

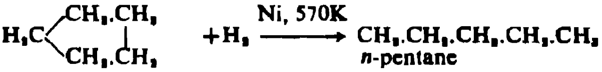


Properties. It is a colourless, pleasant-smelling mobile liquid (b.p. 323K). It is remarkably stable and the ring does not open readily. Various chemical reactions given by it are :

(*i*) Chlorine and bromine give substitution products in presence of light.



(*ii*) On catalytic hydrogenation it undergoes ring fission and gives *n*-pentane.



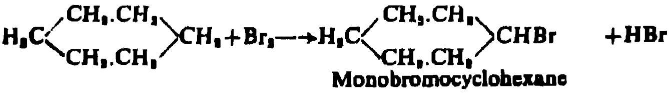
(*iii*) It may be nitrated with conc. HNO_3 in cold or dilute HNO_3 at 370K.

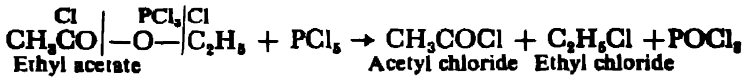
6. **Cyclohexane or Hexamethylene, C_6H_{12}.**—It occurs in petroleum and essential oils. It is manufactured by catalytic hydrogenation of benzene.

$$\underset{\text{Benzene}}{C_6H_6} + 3H_2 \xrightarrow{\text{Ni, 470K}} \underset{\text{Cyclohexane}}{C_6H_{12}}$$

Properties. It is a colourless, pleasant-smelling liquid (b.p. 354K). It is a solvent. Chemically it closely resembles alkanes. Important properties of cyclohexane are :

(*i*) It gives substitution products with chlorine or bromine.





$$\underset{\text{Ethyl acetate}}{\overset{\text{Cl}}{CH_3CO}\Big|-\overset{\text{PCl}_3}{O}-\Big|\overset{\text{Cl}}{C_2H_5}} + PCl_5 \rightarrow \underset{\text{Acetyl chloride}}{CH_3COCl} + \underset{\text{Ethyl chloride}}{C_2H_5Cl} + POCl_3$$

(*iv*) *Reduction*. Reduction of an ester by means of excess of sodium and ethanol gives alcohols.

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + 4[H] \xrightarrow{C_2H_5OH/Na} \underset{\text{Ethanol}}{CH_3CH_2OH} + \underset{\text{Ethanol}}{C_2H_5OH}$$

$$RCOOR' + 4[H] \xrightarrow{C_2H_5OH/Na} RCH_2OH \quad + R'OH \quad (g.)$$

Yield of RCH_2OH increases as the weight of alkyl radical **R′** increases in the molecule of ester taken.

Other reducing agents used are : (*i*) lithium-aluminium hydride and (*ii*) hydrogen under pressure (100-300 atmospheres) in presence of copper chromate (*catalyst*) at 570K.

(*v*) *Alcoholysis* (*splitting by alcohol*). When an ester is refluxed with a large excess of alcohol in presence of a little acid or sodium alkoxide (*catalyst*), the alcohol residue present is replaced by another (a lower one).

$$\underset{\text{Butyl acetate}}{CH_3COOC_4H_9} + C_2H_5OH \overset{C_2H_5ONa}{\rightleftharpoons} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + C_4H_9OH$$

(*vi*) *Acidolysis* (*splitting by acid*). In acidolysis the acid residue present is replaced by another acid residue.

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + \underset{\text{Valeric acid}}{C_4H_9COOH} \rightleftharpoons \underset{\text{Ethyl valerate}}{C_4H_9COOC_2H_5} + \underset{\text{Acetic acid}}{CH_3COOH}$$

5. Uses of Esters.—Esters are used : (*i*) As solvents for cellulose, oils, gums, resins, etc., and as plasticisers.

(*ii*) In making artificial flavours and essences.

SOME INDIVIDUAL MEMBERS

6. Ethyl Acetate, $CH_3COOC_2H_5$.—It can be prepared by any one of the general methods for preparation of esters. It is, however, prepared in the laboratory by *heating ethanol with glacial acetic acid in the presence of concentrated sulphuric acid or dry hydrogen chloride gas.*

$$CH_3CO|\underline{OH + H}|OC_2H_5 \overset{H_2SO_4}{\rightleftharpoons} CH_2COOC_2H_5 + H_2O$$

The acid acts as a protonating agent and serves to remove water as soon as it is formed and thus enables the reversible reaction to proceed to completion.

Expt. A distillation flask is fitted with a dropping funnel and a thermometer. It is connected to the condenser and a receiver as shown in Fig. 26·1. In the distillation flask are taken 50 ml of absolute alcohol with an equal volume of concentrated sulphuric acid. A mixture of 50 ml of absolute alcohol with an equal volume of glacial acetic acid is taken in the dropping funnel. The flask is heated to 413K in an oil bath and the mixture in the funnel is run in at the same rate at which the liquid distils over. The distillate consists of ethyl acetate contaminated with acetic acid, alcohol, water, a little of ether and sulphurous acid.

QUESTIONS

Essay Type :

1. Give a general account of the chemistry of polymethylenes. Show how Baeyer's Strain Theory accounts for the relative stability of such rings.

2. Give general methods of preparing cycloparaffins. Discuss how Baeyer's Strain Theory has explained their relative stability.

3. How are cycloparaffins prepared ? Discuss their stability in the light of Baeyer's Strain Theory and its later developments.
(*Jammu & Kashmir B.Sc. 1971* ; *Punjab 1970*)

4. Describe general methods of preparation of cycloparaffins. Write a short note on their order of stability.

5. Give the preparation of decalin and discuss its geometrical isomerism.

Short Answer Type :

1. Write chemical equations for the reactions, if any, between :

(1) Action of heat on (*i*) calcium adipate ; (*ii*) cyclopropane.

(2) Reduction of (*i*) cyclopentanone ; (*ii*) benzene ; (*iii*) phenol ; (*iv*) cyclopropane ; (*v*) cyclobutane ; (*vi*) cyclobutene.

(3) 1 : 4-dibromobutane+(*i*) metallic sodium ; (*ii*) Disodiomalonic ester followed by hydrolysis and heating.

(4) Cyclohexane+(*i*) Br_2 ; (*ii*) Alkaline $KMnO_4$.

(5) Cyclopentane+(*i*) Br_2 ; (*ii*) HI.

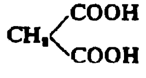
(6) Cyclopropane+ (*i*) Cl_2 ; (*ii*) Br_2 ; (*iii*) HI ; (*iv*) H_2 and Ni.

(7) Cyclobutane+HI.

Appendix I

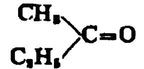
TYPICAL NUMERICAL PROBLEMS

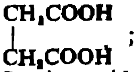
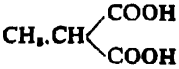
1. Problems on Structural Formula.—Problems based on structural formula require a thorough knowledge of organic compounds and their reactions. Some important reactions commonly associated with unknown compounds and the information given by them are given in the following table :

Reactions	**Inference**
1. Bromine water or 1% alkaline potassium permanganate solution (Baeyer's reagent) is decolorised.	It is an unsaturated compound—an alkene or alkyne.
2. Compound contains C, H & O.	
(*i*) It gives pink colour with Schiff's reagent.	It contains an aldehyde (—CHO) group.
(*ii*) It gives a red ppt. with Fehling's solution and a silver mirror with Tollen's reagent.	It contains an aldehyde (—CHO) group.
(*iii*) It gives an oxime with hydroxylamine and phenylhydrazone with phenylhydrazine but it does not reduce Fehling's solution.	It contains a ketonic (>C═O) group.
(*iv*) It gives an aldehyde on oxidation.	It is a primary alcohol containing characteristic group (—CH_2OH).
(*v*) It gives a ketone on oxidation.	It is a secondary alcohol containing characteristic group (>CHOH).
(*vi*) An effervescence is produced with sodium bicarbonate.	It contains a —COOH group.
(*vii*) A dibasic acid gives CO_2 on heating.	Two —COOH groups are attached to the same carbon atom, *e.g.*,  $CH_2(COOH)_2$ (Malonic acid).
(*viii*) A dibasic acid loses water on heating. (Gives anhydride on heating.)	Two —COOH groups are attached to adjacent carbon atoms, *e.g.*, succinic acid
(*ix*) A hydroxyacid loses water on heating.	It is a β-hydroxyacid, *e.g.*, β-hydroxypropionic acid, which gives acrylic acid on heating.
3. Compounds containing C, H, N & O.	
(*i*) Ammonia is liberated on heating alone or with NaOH or KOH.	It is an amide, ammonium salt of an acid or urea.
(*ii*) Gives a primary amine with bromine and KOH.	It contains an amide (—$CONH_2$) group.

Reactions	**Inference**
4. **Compounds containing C, H & N.**	
Various possibilities are P, S and T-amines, cyanides or isocyanides.	
(*i*) It is soluble in an acid, *e.g.*, HCl.	It may be an amine. (*For distinction between three types of amines see* page 2·312).
(*ii*) On hydrolysis it gives an acid and ammonia.	It is a cyanide.
(*iii*) On hydrolysis with acid, it gives amine and formic acid. No action with alkalis.	It is an isocyanide.
(*iv*) On reduction, it gives a primary amine.	It is a cyanide.
(*v*) On reduction, it gives a secondary amine.	It is an isocyanide.
5. Compound is optically active.	It contains one or more chiral carbon atoms.

2. Isomeric Compounds.—A molecular formula might represent various isomers. Writing of possible isomers represented by a certain molecular formula is the first step. Later on we have to select one of these isomers which corresponds to the various reactions of the compound mentioned in the problem. Some important molecular formulae with possible isomers are given in the table below :

Molecular formula	**Various possible isomers**
(*i*) C_2H_6O	$CH_3.CH_2OH$; $CH_3—O—CH_3$ Ethanol ; Dimethyl ether
(*ii*) $C_4H_{10}O$	$C_2H_5—O—C_2H_5$; $CH_3—O—C_3H_7$; Four isomeric butyl alcohols Diethyl ether ; Methyl propyl ether (*n*- or *iso*-)
(*iii*) C_3H_6O	$CH_3.CH_2.CH=O$: CH_3COCH_3 ; $CH_2=CH.CH_2OH$ Propionaldehyde ; Acetone ; Allyl alcohol
(*iv*) C_4H_8O	C_3H_7CHO Butyraldehyde  $\begin{matrix}CH_3\\C_2H_5\end{matrix}\!>C=O$; An unsaturated alcohol Ethyl methyl ketone
(4) $C_3H_6O_2$	C_2H_5COOH ; $HCOOC_2H_5$; CH_3COOCH_3 Propionic acid ; Ethyl formate ; Methyl acetate
(*vi*) $C_3H_6O_3$	$CH_3CHOH.COOH$; $CH_2OH.CH_2.COOH$ α-hydroxypropionic acid (*Lactic acid*) ; β-hydroxypropionic acid (*Hydracrylic acid*) $(HCHO)_3$ (Metaformaldehyde)
(*vii*) $C_4H_8O_2$	*Acids* : $CH_3.CH_2.CH_2.COOH$; $(CH_3)_2CH.COOH$ *n*-Butyric acid ; *Iso*-Butyric acid *Esters* : $HCOOC_3H_7$; $CH_3COOC_2H_5$; $C_2H_5COOCH_3$ *n*- and isopropyl formate ; Ethyl acetate ; Methyl propionate *Aldol* : $CH_3CHOH.CH_2CHO$ (β-*hydroxybutyraldehyde*)

Molecular formula	Various possible isomers
(*viii*) $C_4H_6O_4$	 $\begin{array}{l}CH_2COOH \\ \vert \\ CH_2COOH\end{array}$; Succinic acid  $CH_3.CH\begin{array}{l}\diagup COOH \\ \diagdown COOH\end{array}$ Isosuccinic acid or Methylmalonic acid
(*ix*) C_2H_7N	$C_2H_5NH_2$; Ethylamine $(CH_3)_2NH$ Dimethylamine
(*x*) C_3H_5N	$C_2H_5C{\equiv}N$; Ethyl cyanide C_2H_5NC Ethyl isocyanide

QUESTIONS

1 Cleavage of a certain ether with an excess of hydriodic acid gives only one alkyl iodide which contains 74·7% of iodine. Hydrolysis of the alkyl iodide gives a secondary alcohol. Find out the structural formula of the ether. (*Delhi B.Sc. 1980*)

2. Hydrolysis of a certain ester gives an acid (A) and an alcohol (B). The acid reduces Fehling's solution Oxidation of alcohol (B) gives an acid identical with (A). Reason out what the ester is. (*Delhi B.Sc. 1980*)

3. An organic compound A gave the following results. C=60·0% ; H=13·33%. On oxidation A gave another product B which on further oxidation gave a mixture of acetic acid and formic acid. What structural formulae would you assign to A and B ? Vapour density of compound A is 30. (*Delhi B.Sc. 1980*)

4. 0·20 g of an organic dibasic acid gave on combustion 0·04 g water and 0·195 g carbon dioxide. The molecular weight of the acid is 90. Assign structural formula to the organic compound. (*Delhi B.Sc. Hons. Sub. 1980*)

5. An ester A whose molecular weight is 116 on hydrolysis gave an acid B and an alcohol C. The acid forms a silver salt containing 59·6% silver. Oxidation of the alcohol C gave a product D which forms an oxime but does not reduce Tollen's reagent. The oxime contains 19·17% of nitrogen. Assign structures to A, B, C and D. Give methods for synthesis of acid B and alcohol C starting from acetylene. (*Delhi B.Sc. Hons. 1979* ; *Allahabad B.Sc. 1972*)

6. An organic compound A on analysis was found to contain C=16·271%, H=0·677% and Cl=72·203%. It reduced Fehling's solution and on oxidation gave a monocarboxylic acid B, having C=14·679% H=0·612% and Cl=65·137%.

On distillation with soda-lime, B gave a sweet smelling liquid C, containing 89·12% chlorine. C can also be obtained by heating A with alkali.

What structural formulae would you assign to A, B and C ? Explain the above reactions. (*Vikram B.Sc. 1979* ; *Delhi 1978*)

7. 0·1588 g of an organic substance (A) gave 0·3615 g CO_2 and 0·1479 g H_2O. Its V.D. was 29. The compound reduces Fehling's solution and on oxidation gives an acid (B), the silver salt of which contained 59·6% Ag. Give the names and structural formulae of A and B and explain the reactions. (*Delhi B Sc. 1979*)

8. An aliphatic organic compound A gave the following results : C=61·01%, H=15·25%, N=23·74%.

On treatment with nitrous acid, A gave another product B which contained C=60%, H=13·33% and no nitrogen. B on careful oxidation gave a compound C which gave iodoform on treatment with iodine and alkali and had a molecular weight 58. What structural formulae would you assign to A, B and C ? Explain the reactions with equations. (*Delhi B.Sc. 1979*)

9. An organic compound A (molecular formu C_4H_9N) on treatment with $NaNO_2$ and dil HCl formed an alcohol B (molecular formula C_4H_8O). The alcohol B on treatment with $I_2/NaOH$ formed iodoform and an unsaturated acid C (molecular formula $C_3H_4O_2$). The acid C on ozonolysis gave formaldehyde and glyoxalic acid.

(*i*) What is the structure of A ?

(*ii*) Write equations for the chemical reactions involved.

(*Delhi B.Sc. Hons. 1981*)

10. Compound A, C_7H_{14} yielded on ozonolysis propanone and 2-butanone. Work out the structural formula and give its name according to the IUPAC system of nomenclature. (*Delhi B.Sc. 1981*)

11. Identify A and B in each of the following sequences of operations :

(*i*) $CH_3CH_2CH_2COOH \xrightarrow{NaOH} A \xrightarrow{\text{Sodalime, }\Delta} B$

(*ii*) $CH_3-\overset{\overset{\large Cl}{|}}{C}H-CH_3 \xrightarrow{\text{alc KOH}} A \xrightarrow[\text{Peroxide}]{HBr} B$

(*iv*) $CH_3CONH_2 \xrightarrow{Br_2/NaOH} A \xrightarrow{HNO_2} B$

(*iv*) $CH_3-C\equiv C-CH_3 \xrightarrow[H_2SO_4]{H_2O,\ Hg^{2+}} A \xrightarrow{[O]} B$ (*Delhi B.Sc. 1981*)

12. Two isomeric neutral substances A and B contain 62·01 % carbon and 10·35% hydrogen. Their vapour density is 29. On mild oxidation, A gives rise to a monobasic acid C, containing 48·64% carbon and 8·11% hydrogen. The equivalent weight of C is found to be 74. On a similar treatment B remains unchanged, but B readily reacts with iodine and sodium hydroxide producing iodoform. What are the structural formulae of A and B ? Write down the equations representing the reactions carried out on A and B as mentioned above. (*Delhi B.Sc. 1981*)

13. An organic compound A of the formula C_3H_6O on treatment with conc. H_2SO_4 gives a neutral compound B of the formula $C_4H_{10}O$.

The compound B on treatment with PCl_5 gives a product which on subsequent treatment with KCN yields a compound C of the formula C_3H_5N. The latter on hydrolysis gives an acid of the formula $C_3H_6O_2$ and on reduction with sodium amalgam gives a base of the formula C_3H_9N. What are the compounds A, B and C ? Write the reactions involved in the transformation of A to the acid, $C_3H_6O_2$ and to the base C_3H_9N. (*Allahabad B.Sc. 1970*

14. An organic compound of molecular formula $C_3H_6Br_2$ yields on hydrolysis a compound A which gives a positive reaction with Schiff's reagent and forms an oxime. Oxidation of A gives B and treatment of B with soda lime yields propane. What are the two possible structures for the original compound ? Discuss the reactions involved. (*Delhi T.D.C. II 1972*)

15. An unsaturated hydrocarbon contains six carbon atoms in the molecule and has the molecular weight 80. Write the possible structures for the hydrocarbon and give one reaction of each of the structures. (*Delhi B.Sc. Hons. 1972*)

16. A hydrocarbon having the molecular formula $C_{10}H_{16}$ gave on ozonolysis one molecule of acetone, two molecules of formaldehyde and one molecule of $OHC-CH_2-CH_2-CO-CHO$. Write all the possible structures for the hydrocarbon and give their IUPAC names. (*Delhi B.Sc. Hons. 1972*)

17. An alcohol A (vapour density 30) gave, on dehydration, a hydrocarbon B, containing C, 85·7% and H, 14·3%. B on successive reactions with hydrogen iodide and moist silver oxide gave C which is isomeric with A. When C is

treated with phosphorus pentachloride D was obtained which contained Cl, 45·2%. Explain these reactions and assign structures to A, B, C and D.
(Delhi B.Sc. Hons. 1980, 72)

18. An organic compound A contains carbon = 29·27%, hydrogen = 5·69% and the rest is bromine. On treatment with alcoholic potash, it gives a compound B, containing 85·7% carbon and 14·3% hydrogen. B on treatment with hydrogen bromide yields another compound C, which is isomeric with A. Identify A, B and C. Write equations for the corresponding reactions. *(Delhi B.Sc. 1974)*

19. A compound X of the formula $C_4H_8Cl_2$ undergoes hydrolysis giving another compound Y which does not contain chlorine and which forms an oxime, but does not reduce Fehling's solution. Write the structural formulae of the two compounds. *(Madras B.Sc. 1978)*

20. An organic compound A containing 40% of carbon, 6·67% of hydrogen and vapour density 15, reduces Fehling's solution and restores the colour of Schiff's reagent. On treatment with caustic potash, it gave an alcohol B, that could be obtained by the reduction of A and an acid C which could be obtained by the oxidation of A. What was the compound A ? Explain these reactions.
(Agra B.Sc. 1980 ; Delhi 1978 Supp. ; Gorakhpur 1978)

21. An organic compound (A) mol formula C_3H_7NO insoluble in dilute acids did not respond to haloform reaction. This (A) on treatment with Br_2/KOH formed a basic nitrogenous compound (B) mol formula C_2H_7N. B on treatment with HNO_2 formed an alcohol (C) mol formula C_2H_6O. C on treatment with I_2/NaOH gave iodoform. Suggest the possible structures of A, B, and C. How can compound A be prepared from acrylic acid ? *(Delhi B Sc. 1978 Supp.)*

22. An organic compound (A) was found to contain C = 39·13% and H = 8·70%, vapour density = 46. It gave the following reactions :

(*i*) Oxidation with HNO_3 gave a dibasic acid, B.

(*ii*) With P_2O_5 it gave an unsaturated aldehyde, C.

(*iii*) With PCl_5 it gave a chlorinated hydrocarbon (V. D. 73·5), D.

Assign the structural formula for A, B, C, and D.
(Delhi B.Sc. 1978 Supp.)

23. A hydrocarbon (A) on monochlorination yielded a compound C_4H_9Cl (B) which when refluxed over metallic sodium yielded 2,2,3,3-tetramethylbutane. What is the structure of A and B ?
(Delhi B.Sc. Hons. Sub. 1978)

24. An unsaturated hydrocarbon reacts with HCl to give a product that is identical with the product obtained from treating propanone with PCl_5. Derive the structure of the unsaturated hydrocarbon.
(Delhi B.Sc. Hons. Sub. 1978)

25. A compound (A) of the formula $C_4H_{10}O$ undergoes oxidation to give a compound (B) C_4H_8O. B forms an oxime but does not reduce Fehling's solution. B reacts with iodine and potassium hydroxide to form iodoform. Derive the structures of A and B and explain the reactions.
(Delhi B Sc. Hons. Sub. 1978)

26. An organic compound (A) molecular formula $C_3H_6O_2$, when treated with excess of ammonia and then heated formed (B), molecular formula C_3H_7ON. B when treated with P_2O_5 formed (C), molecular formula C_3H_5N. C, on complete acid hydrolysis formed A.

C on reduction with complex metal hydride formed a basic nitrogenous compound (D), molecular formula C_3H_9N. D on treatment with HNO_2 formed an alcohol (E), molecular formula C_3H_8O. E on oxidation formed compound A.

Give the structures of compounds A, B, C, D and E and explain the various chemical reactions involved. *(Delhi B.Sc. 1978)*

27. A compound having molecular formula $C_6H_{12}O$ reacted with hydroxylamine but did not reduce Tollen's reagent. Reduction with hydrogen and platinum gave an alcohol which was dehydrated to give chiefly a single alkene. Ozonisation and decomposition of the ozonide gave two liquid products, one of which reduced Tollen's reagent but did not give a positive iodoform test, whereas the other did not reduce Tollen's reagent but did give a positive iodoform test. Give the structure of the original compound and show the reactions that it undergoes. *(Delhi B.Sc. Hons. 1978)*

28 There are four isomeric alcohols of molecular formula $C_4H_{10}O$. Which of these alcohols is indicated by the following experimental observations ? Compound D ($C_4H_{10}O$), On oxidation by potassium permanganate in acid solution, gives compound E ($C_4H_8O_2$), a carboxylic acid. Treatment of compound D with warm phosphoric acid brings about dehydration and yields compound F (C_4H_8) Treatment of compound F with warm aquenus sulphuric acid gives G ($C_4H_{10}O$), a new alcohol isomeric with compound D. Compound G is resistant to oxidation. Propose structures for compounds D,E,F, and G consistent with these observations. (*Punjab B.Sc. 1977*)

29. An organic compound gave the following results :

C=69·77% and H=11·62%

Its vapour density was found to be 43. It gave a crystalline derivative with sodium besulphite but did not reduce Fehling's solution. On oxidation it gave a mixture of acetic acid and propionic acid Deduce its possible structures and name shem. (*Delhi B.Sc. Hons. Sub. 1982*)

30. An organic compound A gave the following results on analysis :

C=62·07, H=10·35% and the rest is oxygen.

Its vapour density is 29. It forms an acetyl derivative with acetic anhydride and decolorises bromine water. Name the compound and explain the above reactions. Write down all possible isomers of A and distinguish between them. (*Meerut B.Sc. 1980*)

31. An organic compound A molecular formula C_3H_7NO gave the following reactions :

(*a*) With HNO_2 gave the fatty acid B which is also obtainable by the action of dilute HCl on A

(*b*) With P_2O_5 gave a compound C with molecular formula C_3H_5N.

(*c*) With excess of KOH solution and Br_2 formed D which when reacted with chloroform and alkali, produced a bad smelling substance E.

Explain the reactions and assign structures to A, B, C, D and E. (*Meerut B Sc., 1979*)

32. A compound (A) has 85·7% C and 14·0% H. The vapour density of (A) is 28. (A) reacts with ozone and forms another compound (B) which contains 46·1% C, 7 7% H and 46·2% oxygen. (B) reacts with hydrogen in presence of platinum to produce acetaldehyde. Explain the structures of A and B. (*Agra B.Sc. 1978*)

33. 0·1588g of an organic compound on combustion forms 0·3615 g of of CO_2 and 0·1479 g of water. Its V.D. is 29 The compound reduces Fehling's solution and on oxidation forms an acid, the silver salt of which contains 59 6% of silver. Give the structural formula and name of the compound. (*Bhopal B.Sc. 1976*)

34. A dibasic acid gave the following results on analysis :

(*i*) 0·354 g of the acid gave on combustion 0 5284 g of CO_2 and 0·162 g of water.

(*ii*) 0·5976 g of its silver salt left on ignition 0·3888 g of silver.

Determine the molecular formula of the acid and write down the structural formulae of its possible isomers. (*Kanpur B Sc. 1980*)

35. A monobasic acid A gave the following results :

C=40%, H=6·67%, O=53·33%.

0·985 g silver salt of this acid gave 0·54 g of silver on ignition.

When the acid A was heated, it was converted into another monobasic acid B by loss of water. B contained C=50%, H=5·55%, O=44·45% and its V.D.=36. It gave a dihydroxy acid C on treatment with alkaline $KMnO_4$ solution.

When treated with HI the acid B was converted into another monobasic

36. Two organic compounds A and B contain C=40% and H=6·66%. V.D. of A is 15 and that of B is 30. A reduces Fehling's solution while B does not reduce Fehling's solution but liberates carbon dioxide with sodium carbonate. Explain these reactions and give structural formulae of A and B. *(Jiwaji B.Sc. 1980)*

37. An organic compound A has C=65·45% H=9·1% and N=25·45%

Its vapour density is 27·5. A on hydrolysis gives NH_3 and another compound B with mol. wt. =74 having C=48·6% and H=8·1%. (A) on reduction gives a monoacid base C with mol. wt=59.

Explain these reactions and write the structures of compounds A, B, C. *(Vikram B.Sc. 1979)*

38. A pure hydrocarbon of the formula C_6H_{12} decolorises bromine water and disolves in conc. H_2SO_4. It yields *n*-hexane on hydrogenation and on oxidation with excess $KMnO_4$ gives a mixture of two acids of the type RCOOH. What is its structure? *(Guru Nanak Dev B.Sc. 1982)*

39. A compound having molecular formula $C_6H_{12}O$ reacted with hydroxylamine but did not reduce Tollen's reagent. Reduction with hydrogen and platinum gave an alcohol which was dehydrated to give chiefly a single alkene. Ozonisation and decomposition of the ozonide gave two liquid products, one of which reduced Tollen's reagent but did not give a positive iodoform test whereas the other did not reduce Tollen's reagent but gave a positive iodoform test. Give the structure of the original compound and show the reactions that it undergoes. *(Delhi B. Sc. Hons. 1982)*

40. An organic compound A, C_3H_5N on boiling with alkali gives ammonia and sodium salt of an acid B, $C_3H_6O_2$. A on reduction gives C, C_3H_9N which with nitrous acid gives D, C_3H_8O. Give the structural formulae for compounds A, B, C and D Describe a method of preparation for A. *(Delhi B.Sc. 1982)*

41. An organic compound A on analysis is found to contain C=60% and H=13·33%. Its V.D. is 30. On oxidation it gave a compound B containing C=62·07% and H=10·35%. Compound B reduces Fehling's solution but does not give iodoform test. Give the names and structural formulae of A and B and explain the reactions. *(Delhi B.Sc. 1982)*

42. An alcohol $C_5H_{11}OH$ on oxidation gives a ketone having five carbon atoms. When the alcohol is dehydrated and the resulting alkene is oxidised, a mixture of a ketone and a carboxylic acid results. What is the alcohol? *(Rajasthan B.Sc. 1978)*

43. A hydrocarbon (A) decolourises bromine and in the presence of platinum catalyst adds a molecule of hydrogen to give *n*-hexane. When (A) is oxidised vigorously with $KMnO_4$, a single carboxylic acid containing three carbon atoms is isolated. Give the name and structure of (A) and explain the reactions. *(Maharishi Dayanand B.Sc. 1979)*

44. Suggest suitable structure for an organic compound (A)—($C_6H_{14}O$) which gives rise to the following reactions. Suggest appropriate structure for (B) based on the reactions given below :

(*a*) Compound (A) $\xrightarrow{H_2SO_4,\ \Delta}$ Compound (B)

(*b*) Compound (B) $\xrightarrow{Br_2 \text{ in } CCl_4}$ Dibromide of (B)

(c) Compound (B) $\xrightarrow{O_3}$ Its Ozonide $\xrightarrow{Zn,\ H_2O}$ Propionaldehyde + Acetone *(Madras B.Sc. 1979)*

45. An organic compound gave the following results on combustion analysis : 0·365 g of the compound produced 0·88g of carbon dioxide, and 0·495 g of water. Further, in a Dumas' nitrogen estimation experiment

0·1186g of the substance gave 20 ml of nitrogen measured at 27°C and 760 mm pressure. The vapour density of the compound is found to be 36·5. Determine the molecular formula of the compound. (*Nagpur B.Sc. 1979*)

46. An alkylene dibromide X ($C_6H_{10}Br_2$) on dehydrobromination with excess of $NaNH_2$ gave rise to a compound Y (C_6H_{10}). Compound Y on hydration furnished compound Z which has the following structure :

$$(CH_3)_2CH-CH_2-CO-CH_3$$

Suggest suitable structural formulae for (X and Y) that are consistent with the above stated facts. (*Madras B.Sc. 1979*)

47. A compound (A) contains C=30·5%, H=3·9% and Cl=45·2%. On catalytic reduction with Pd and $BaSO_4$ it gives (B), which reacts with hydroxylamine and also reduces Fehling's solution. B, on treatment with aqueous KOH gives (C) with the same empirical formula as that of (B). (C) on catalytic hydrogenation gives (D), which on dehydration gives a synthetic rubber intermediate of molecular formula C_4H_6. Identify (A), (B), (C), and (D) and explain the reactions. (*Rajasthan B.Sc. 1978*)

48. An organic compound (A) contains C=32%, H=6·66%, and N=18·67%. On reduction it gave a primary amine (B), which gave ethyl alcohol with nitrous acid. (B) gave an offensive smell on warming with chloroform and KOH and gave another compound (C), which on reduction gave ethylmethylamine. What structural formulae would you assign to (A), (B), and (C)? Explain the reactions also. (*Kurukshetra B.Sc., 1979*)

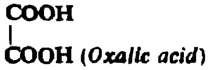
ANSWERS

1. $(CH_3)_2CH-O-CH(CH_3)_2$ (*Di-isopropyl ether*)

2. $HCOOCH_3$ (*Methyl formate*)

3. $$\underset{\text{Isopropyl alcohol (A)}}{(CH_3)_2CHOH} \xrightarrow{O} \underset{\text{Acetone (B)}}{(CH_3)_2C=O} \xrightarrow{O} CH_3COOH+HCOOH$$

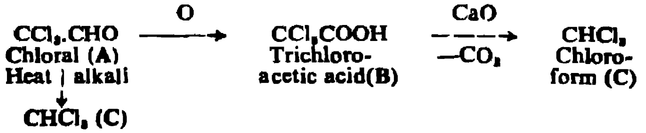
4.



$$\begin{array}{l}COOH\\ |\\ COOH\end{array}$$ (*Oxalic acid*)

5. A is $C_2H_5COOCH(CH_3)_2$ (*Isopropyl propionate*)
   B is C_2H_5COOH (*Propionic acid*)
   C is $(CH_3)_2CHOH$ (*Isopropyl alcohol*)
   D is $CH_3.CO.CH_3$ (*Acetone*)

6.



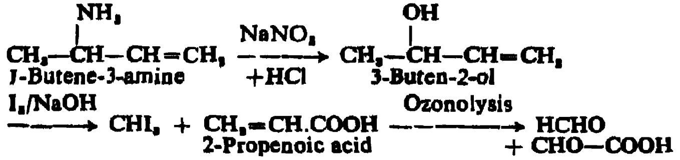
$$\underset{\text{Chloral (A)}}{CCl_3.CHO} \xrightarrow{O} \underset{\text{Trichloro-acetic acid(B)}}{CCl_3COOH} \xrightarrow[-CO_2]{CaO} \underset{\text{Chloroform (C)}}{CHCl_3}$$

$$CCl_3.CHO \xrightarrow{\text{Heat | alkali}} CHCl_3\ (C)$$

7. A is C_2H_5CHO (*Propionaldehyde*)
   B is C_2H_5COOH (*Propionic acid*)

8. $$\underset{\text{(A)}}{\underset{\text{Isopropylamine}}{(CH_3)_2CHNH_2}} \xrightarrow{HONO} \underset{\text{alcohol (B)}}{\underset{\text{Isopropyl-}}{(CH_3)_2CHOH}} \xrightarrow{O} \underset{\text{Acetone (C)}}{CH_3COCH_3} \xrightarrow{I_2/NaOH} \underset{\text{form}}{\underset{\text{Iodo-}}{CHI_3}}$$

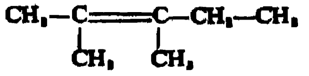
9.



$$\underset{\text{1-Butene-3-amine}}{CH_3-\overset{\overset{NH_2}{|}}{C}H-CH=CH_2} \xrightarrow[+HCl]{NaNO_2} \underset{\text{3-Buten-2-ol}}{CH_3-\overset{\overset{OH}{|}}{C}H-CH=CH_2}$$

$$\xrightarrow{I_2/NaOH} CHI_3 + \underset{\text{2-Propenoic acid}}{CH_2=CH.COOH} \xrightarrow{\text{Ozonolysis}} HCHO + CHO-COOH$$

10.



$$CH_3-\underset{\underset{CH_3}{|}}{C}=\underset{\underset{CH_3}{|}}{C}-CH_2-CH_3$$

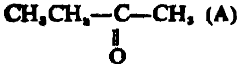
2, 3-Dimethyl-2-pentene

11. (*i*) $CH_3CH_2CH_2COONa$ (A) ; $CH_3CH_2CH_3$ (B)
Sod. butyrate ; Propane

(*ii*) $CH_3{-}CH{=}CH_2$ (A) ; $CH_3{-}CH_2{-}CH_2Br$ (B)
Propene ; 1-Bromopropane

(*iii*) CH_3NH_2 (A) ; CH_3OH (B)
Methylamine ; Methanol

(*iv*)



$CH_3CH_2{-}\underset{\underset{O}{\|}}{C}{-}CH_3$ (A) ; CH_3COOH (B)
2-Butanone ; Acetic acid

12. A is C_2H_5CHO (Propanal)

B is CH_3COCH_3 (Propanone)

$$\underset{(A)}{C_2H_5CHO} \xrightarrow{O} \underset{(C)}{C_2H_5COOH}$$

$$\underset{(B)}{CH_3COCH_3} \xrightarrow{I_2/NaOH} CHI_3 + CH_3COONa$$

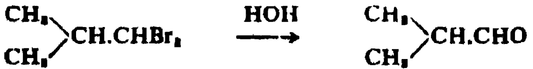
13.

$$\begin{tikzcd} \underset{\text{(A)}}{\underset{\text{Ethanol}}{C_2H_5OH}} \arrow[r, "H_2SO_4"] & \underset{\text{(B)}}{\underset{\text{Diethyl ether}}{C_2H_5.O.C_2H_5}} \arrow[r, "PCl_5"] & \underset{\text{Ethyl chloride}}{C_2H_5Cl} \arrow[d, "KCN"] \\ & \underset{\text{Propionic acid}}{C_2H_5COOH} & \underset{\text{(C)}}{\underset{\text{Ethyl cyanide}}{C_2H_5CN}} \arrow[l, "2HOH", "-NH_3"'] \arrow[d, "4H"', "Na/Hg"] \\ & & \underset{n\text{-Propylamine}}{C_2H_5CH_2NH_2} \end{tikzcd}$$

14 Compounds : (*i*) $\underset{\text{1, 1-dibromobutane}}{CH_3CH_2CH_2CHBr_2} \xrightarrow{HOH} \underset{\text{Butanal (A)}}{CH_3CH_2CH_2CHO}$

$$\xrightarrow{O} \underset{\text{Butanoic acid (B)}}{CH_3CH_2CH_2COOH} \xrightarrow{\text{Soda lime}} \underset{\text{Propane}}{CH_3.CH_2.CH_3}$$

(*ii*)



$(CH_3)_2CH.CHBr_2 \xrightarrow{HOH} (CH_3)_2CH.CHO$

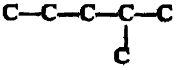
1, 1-dibromo-2-methyl propane ; A

$$\xrightarrow{O} \underset{B}{(CH_3)_2CHCOOH} \xrightarrow{\text{Soda-lime}} CH_3.CH_2.CH_3$$

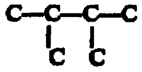
15. Molecular formula C_6H_8. Write different isomeric structures for the various possible ways in which 3 double bonds or one double bond and one triple bond can be introduced in the following skeletons :

(*i*) C—C—C—C—C—C

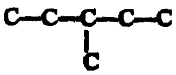
(*ii*)

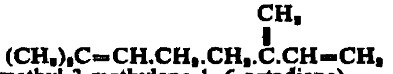


(*iii*)

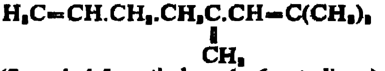


(*iv*)

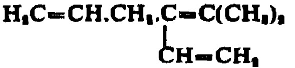


16. (*i*)

$(CH_3)_2C{=}CH.CH_2.CH_2.\overset{CH_2}{\overset{\|}{C}}.CH{=}CH_2$

(7-methyl-3-methylene-1, 6-octadiene)

(*ii*)

$H_2C{=}CH.CH_2.CH_2\underset{CH_2}{\underset{\|}{C}}.CH{=}C(CH_3)_2$

(7-methyl-5-methylene-1, 6-octadiene)

(*iii*)

$H_2C{=}CH.CH_2.\underset{CH=CH_2}{\underset{|}{C}}{=}C(CH_3)_2$

(5-methyl-4-vinyl-1, 4-hexadiene)

17. $\underset{\text{1-Propanol (A)}}{CH_3.CH_2.CH_2OH} \xrightarrow{-H_2O} \underset{\text{Propylene (B)}}{CH_3.CH{=}CH_2} \xrightarrow{HI} \underset{\text{2-Iodopropane}}{CH_3.CHI.CH_3}$

$\xrightarrow{AgOH} \underset{\text{2-Propanol (C)}}{CH_3.CHOH.CH_3} \xrightarrow{PCl_5} \underset{\text{2-Chloropropane (D)}}{CH_3.CHCl.CH_3}$

18. $\underset{\text{A (1-Bromopropane)}}{CH_3.CH_2.CH_2Br} \xrightarrow[\text{alc.}]{KOH} \underset{\text{B (Propene)}}{CH_3.CH{=}CH_2}$

$\xrightarrow{HBr} \underset{\text{C (2-Bromopropane)}}{CH_3.CHBr.CH_3}$ (an isomer of A)

19. X is $CH_3.CCl_2.C_2H_5$ (2, 2-dichlorobutane)
Y is $CH_3.CO.C_2H_5$ (2-Butanone)

20. A is HCHO (formaldehyde)
B is CH_3OH (Methanol)
C is HCOOH (formic acid)

$\underset{A}{HCHO}+NaOH \longrightarrow \underset{B}{CH_3OH} + \underset{\text{sod. salt of C}}{HCOONa}$

21. A is $C_2H_5CONH_2$ (Propionamide)
B is $C_2H_5NH_2$ (Ethylamine)
C is C_2H_5OH (Ethyl alcohol)

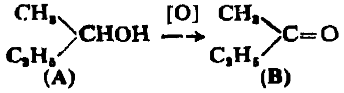
22. A is CH_2OH . CHOH . CH_2OH (Glycerol)
B is HOOC—COOH (Oxalic acid)
C is $CH_2{=}CH.CHO$ (Acrolein)
D is $CH_2Cl.CHCl.CH_2Cl$ (1, 2, 3-Trichloropropane)

23. A is $(CH_3)_2$ CH—CH_3 (isobutane or 2-methylpropane)
B is $(CH_3)_3CCl$ (*tert.* butyl chloride or 2-chloro-2-methylpropane)

24. CH_3—C≡CH (Propyne)

$CH_3.C{\equiv}CH \xrightarrow{HCl} CH_3.CCl_2\,.\,CH_3 \xleftarrow{PCl_5} CH_3.CO.CH_3$

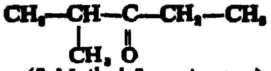
25. A is $C_2H_5CHOH.CH_3$ (2-Butanol)
B is $C_2H_5COCH_3$ (2-Butanone)



$CH_3COC_2H_5 + 3I_2{+}4KOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + C_2H_5COOK + 3KI + 3H_2O$

26. A is C_2H_5COOH (Propionic acid)
B is $C_2H_5CONH_2$ (Propionamide)
C is C_2H_5CN (Ethyl cyanide)
D is $C_2H_5CH_2NH_2$ (Propylamine)
E is $C_2H_5CH_2OH$ (1-Propanol)

27. Original compound is



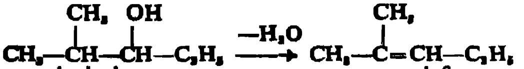
$$CH_3-\underset{CH_3}{\underset{|}{CH}}-\underset{O}{\underset{\|}{C}}-CH_2-CH_3$$

(2-Methyl-3-pentanone)

Reactions :

(*i*) It gives oxime but does not reduce Tollen's reagent. It suggests a carbonyl group which is not an aldehyde group.

(*ii*) On reduction it gives an alcohol. 2-Methyl-3-pentanol which on dehydration gives an alkene, 2-Methyl-2-pentene. This being highly branched is most stable and hence obtained as major product



$$CH_3-\overset{CH_3}{\overset{|}{CH}}-\overset{OH}{\overset{|}{CH}}-C_2H_5 \xrightarrow{-H_2O} CH_3-\overset{CH_3}{\overset{|}{C}}=CH-C_2H_5$$

alcohol olefin

(*iii*) On ozonolysis olefin gives $(CH_3)_2C=O$ (*acetone*) and C_2H_5CHO (*propionaldehyde*)—two liquid products.

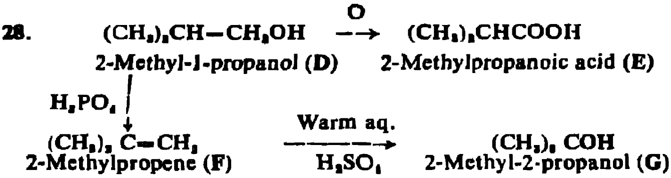
C_2H_5CHO reduces Tollen's reagent but does not give iodoform test.

$$C_2H_5CHO+2Ag(NH_3)_2^+ +3OH^- \longrightarrow C_2H_5COO^- +2Ag+4NH_3+2H_2O$$

CH_3COCH_3 gives iodoform test but does not reduce Tollen's reagent.

$$CH_3COCH_3+3I_2+2Na_2CO_3 \longrightarrow CHI_3+CH_3COONa+3NaI+2CO_2+H_2O$$

28.



$$(CH_3)_2CH-CH_2OH \xrightarrow{O} (CH_3)_2CHCOOH$$

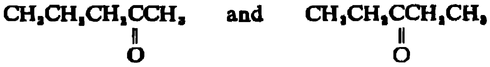
2-Methyl-1-propanol (D) 2-Methylpropanoic acid (E)

$$\downarrow H_3PO_4$$

$$(CH_3)_2C=CH_2 \xrightarrow[H_2SO_4]{\text{Warm aq.}} (CH_3)_3COH$$

2-Methylpropene (F) 2-Methyl-2-propanol (G)

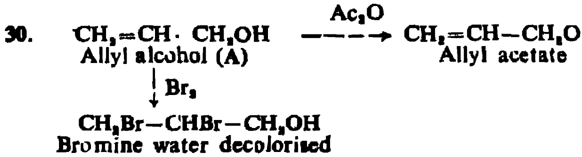
29.



$$CH_3CH_2CH_2\underset{O}{\underset{\|}{C}}CH_3 \quad \text{and} \quad CH_3CH_2\underset{O}{\underset{\|}{C}}CH_2CH_3$$

2-Pentanone 3-Pentanone

30.



$$CH_2=CH\cdot CH_2OH \xrightarrow{Ac_2O} CH_2=CH-CH_2OOCCH_3$$

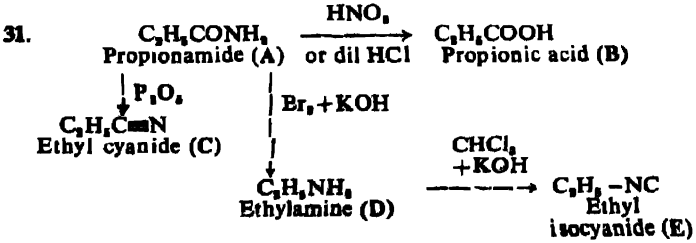
Allyl alcohol (A) Allyl acetate

$$\downarrow Br_2$$

$$CH_2Br-CHBr-CH_2OH$$

Bromine water decolorised

31.



$$C_2H_5CONH_2 \xrightarrow[\text{or dil HCl}]{HNO_2} C_2H_5COOH$$

Propionamide (A) Propionic acid (B)

$$\downarrow P_2O_5$$

$$C_2H_5C\equiv N$$

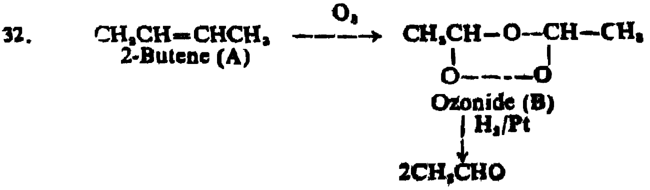
Ethyl cyanide (C)

$$\downarrow Br_2+KOH$$

$$C_2H_5NH_2 \xrightarrow{CHCl_3 + KOH} C_2H_5-NC$$

Ethylamine (D) Ethyl isocyanide (E)

32.



$$CH_3CH=CHCH_3 \xrightarrow{O_3} CH_3CH-O-CH-CH_3$$

2-Butene (A)

$$\underset{O---O}{}$$

Ozonide (B)

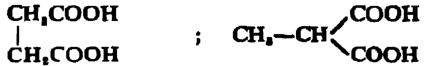
$$\downarrow H_2/Pt$$

$$2CH_3CHO$$

33. $CH_3.CH_2.CH=O$ (Propanal)

34. Mol formula $C_4H_6O_4$

Possible isomers :

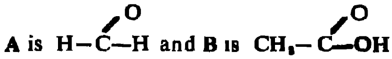


$$\underset{\text{Succinic acid}}{\begin{matrix}CH_2COOH\\ |\\ CH_2COOH\end{matrix}} \; ; \; \underset{\text{Methylmalonic acid}}{CH_3-CH(COOH)_2}$$

35.
$$\underset{\substack{\beta\text{-Hydroxypropionic acid}\\ \text{(A)}}}{CH_2OH.CH_2.COOH} \xrightarrow[-H_2O]{\text{Heat}} \underset{\text{Acrylic acid (B)}}{CH_2=CH.COOH}$$

$$\text{(B)} \xrightarrow{\text{Alk. } KMnO_4} \underset{\substack{\text{2, 3-Dihydroxypropionic acid}\\ \text{(glyceric acid)—(C)}}}{CH_2OH.CHOH.COOH}$$

$$\text{(B)} \xrightarrow{HI} \underset{\substack{\beta\text{-iodopropionic}\\ \text{acid (D)}}}{CH_2I-CH_2-COOH}$$



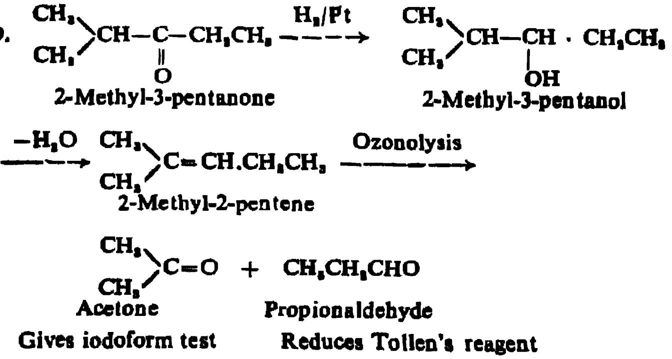
36. A is $H-\overset{O}{\overset{\|}{C}}-H$ and B is $CH_3-\overset{O}{\overset{\|}{C}}-OH$

37.
$$\underset{\substack{\text{Ethyl}\\ \text{cyanide (A)}}}{C_2H_5C\equiv N} \xrightarrow[-NH_3]{H_2O} \underset{\substack{\text{Propionic}\\ \text{acid (B)}}}{C_2H_5COOH}$$

$$\text{(A)} \xrightarrow{H} \underset{\text{Propylamine (C)}}{C_2H_5CH_2NH_2}$$

38.
$$\underset{\text{2-Hexene}}{CH_3.CH_2.CH_2.CH=CH.CH_3} \xrightarrow{KMnO_4} CH_3CH_2CH_2COOH + CH_3COOH$$

(Two acids of the type RCOOH)



39.
$$\underset{\text{2-Methyl-3-pentanone}}{(CH_3)_2CH-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2CH_3} \xrightarrow{H_2/Pt} \underset{\text{2-Methyl-3-pentanol}}{(CH_3)_2CH-\underset{\underset{\displaystyle OH}{|}}{CH}\cdot CH_2CH_3}$$

$$\xrightarrow{-H_2O} \underset{\text{2-Methyl-2-pentene}}{(CH_3)_2C=CH.CH_2CH_3} \xrightarrow{\text{Ozonolysis}}$$

$$\underset{\text{Acetone}}{(CH_3)_2C=O} + \underset{\text{Propionaldehyde}}{CH_3CH_2CHO}$$

Gives iodoform test Reduces Tollen's reagent

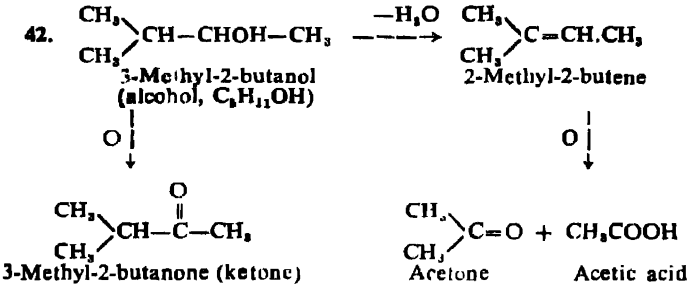
40.
$$\underset{\text{Ethyl cyanide (A)}}{C_2H_5C\equiv N} \xrightarrow[-NH_3]{\text{Hot Alkali}} \underset{\text{Propionic acid (B)}}{C_2H_5COOH}$$

$$\text{(A)} \xrightarrow{H} \underset{\text{Propylamine (C)}}{C_2H_5CH_2NH_2} \xrightarrow{HONO} \underset{\text{1-Propanol (D)}}{C_2H_5CH_2OH}$$

41. A is $CH_3CH_2CH_2OH$ (1-Propanol)

B is CH_3CH_2CHO (Propanal)

42.



43. $CH_3.CH_2.CH=CH.CH_2.CH_3 \xrightarrow{H_2/Pt} CH_3CH_2CH_2CH_2CH_2CH_3$

3-Hexene $\qquad$ *n*-Hexane

$\downarrow$ O

$2\ CH_3.CH_2.COOH$

Propionic acid (*Two molecules*)

44. $CH_3CH_2CHOH.CH(CH_3)_2 \xrightarrow[\Delta]{H_2SO_4} CH_3CH_2CH=C(CH_3)_2$

2-Methyl-3-pentanol (A) $\qquad$ 2-Methyl-2-pentene (B)

45. $C_4H_{11}N$

46. $(CH_3)_2CH.CH_2.CHBr\text{-}CH_2Br \xrightarrow[NaNH_2]{-2HBr} (CH_3)_2CH.CH_2.C\equiv CH$

1, 2-Dibromo-4-methylpentane (X) $\qquad$ 4-Methyl-1-pentyne (Y)

47. $CH_3COCl \xrightarrow{Pd/BaSO_4} CH_3CHO$

Acetyl chloride (A) $\qquad$ Acetaldehyde (B)

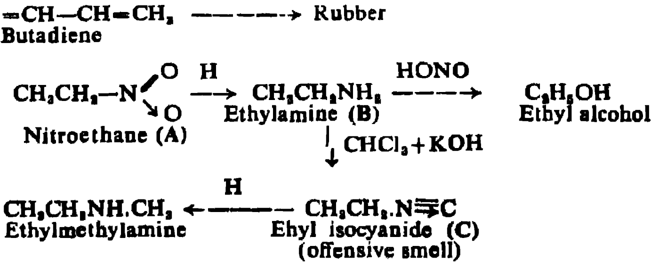
$\xrightarrow{aq\ KOH} CH_3CHOH-CH_2CHO \xrightarrow{H_2} CH_3CHOHCH_2CH_2OH$

Aldol (C) $\qquad$ 1,3-butanediol

$\xrightarrow{-2H_2O} CH_2=CH-CH=CH_2 \longrightarrow$ Rubber

1,3-Butadiene

48.



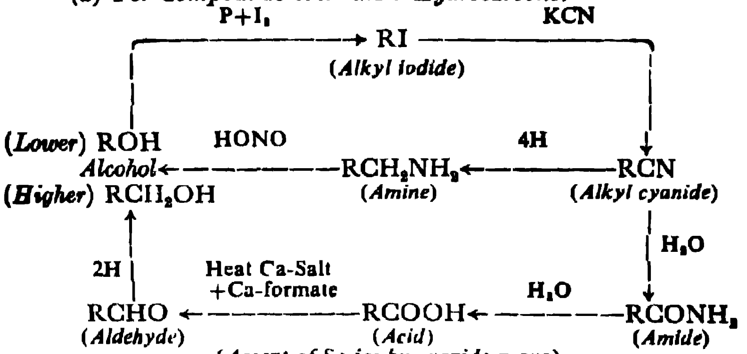
$CH_3CH_2-NO_2 \xrightarrow{H} CH_3CH_2NH_2 \xrightarrow{HONO} C_2H_5OH$
Nitroethane (A)
Ethylamine (B)
Ethyl alcohol
$CHCl_3 + KOH$
$CH_3CH_2NH.CH_3 \xleftarrow{H} CH_3CH_2.N\equiv C$
Ethylmethylamine
Ehyl isocyanide (C)
(offensive smell)

Appendix 2

TYPICAL CONVERSIONS

1. **Ascent of Series.**—*Conversion of an organic compound into its next higher homologue is termed* **Ascent of Series.** The carbon atom is introduced into the chain in the form of a cyanide group or by *Wurtz Synthesis* especially in hydrocarbons. The chain of reactions involved in the change is summarised below :

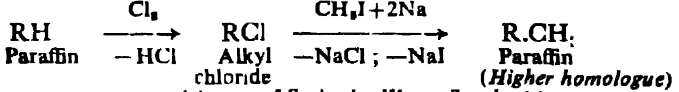
(*a*) *For Compounds other than Hydrocarbons.*



(*Ascent of Series by cyanide group*)

As indicated above, suppose we start with an alcohol ROH and go round the chain once (either *via* amine or *via* acid), we get the next higher homologue RCH_2OH. Go round the chain again, we get still next higher homologue $RCH_2.CH_2OH$. In fact we can start with any member of the chain and get the next higher homologue by going round the chain once.

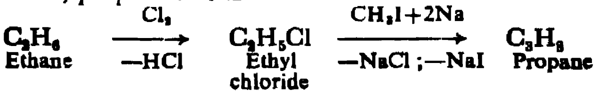
(*b*) *For Hydrocarbons.*



$$\underset{\text{Paraffin}}{RH} \xrightarrow[-HCl]{Cl_2} \underset{\text{Alkyl chloride}}{RCl} \xrightarrow[-NaCl\ ;\ -NaI]{CH_3I+2Na} \underset{\text{Paraffin (Higher homologue)}}{R.CH_3}$$

(*Ascent of Series by Wurtz Synthesis*)

For example, ethane can be converted into its next higher member, propane as indicated below :



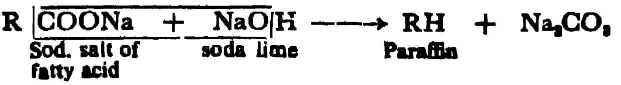
$$\underset{\text{Ethane}}{C_2H_6} \xrightarrow[-HCl]{Cl_2} \underset{\text{Ethyl chloride}}{C_2H_5Cl} \xrightarrow[-NaCl\ ;-NaI]{CH_3I+2Na} \underset{\text{Propane}}{C_3H_8}$$

2. **Descent of Series.**—*Conversion of an organic compound into its next lower homologue is called* **Descent of Series.** This is effected by making use of *either*

(*i*) *Hofmann's Bromamide reaction* wherein an amide is treated with bromine and caustic potash and the amine obtained contains one atom of carbon less than the amide

$$RCONH_2 \xrightarrow{Br_2+KOH} RNH_2$$

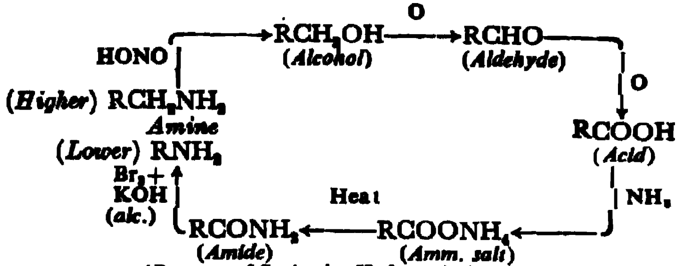
or (*ii*) The reaction—*heating sodium salt of a fatty acid with soda lime*—wherein the paraffin obtained contains one carbon atom less than the acid.



$$R\,\underset{\text{Sod. salt of fatty acid}}{\overline{|COONa}} + \underset{\text{soda lime}}{\overline{NaO|}}H \longrightarrow \underset{\text{Paraffin}}{RH} + Na_2CO_3$$

The chain of reactions involved for getting a lower homologue is summarised below :

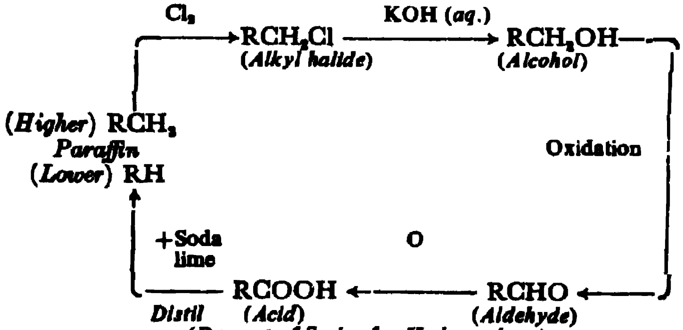
(*a*) ***For compounds other than Paraffins.***



(*Descent of Series by Hofmann's Reaction*)

As indicated above suppose we start with an amine RCH_2NH_2 and go round the chain once, we get the next lower homologue, RNH_2. In fact we can start with any member of the chain and get the next lower homologue by going round the chain once.

(*b*) ***For Paraffins***

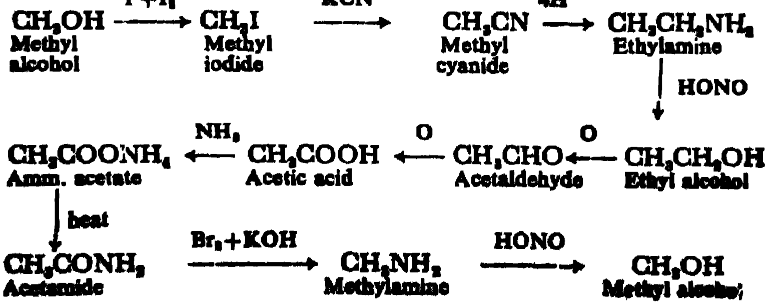


(*Descent of Series for Hydrocarbons*)

A paraffin is easily converted into its next lower homologue by following the chain of reactions given above.

3. Typical Examples of Ascent and Descent of the Series.

(1) Conversion of Methyl alcohol (Methanol) into Ethyl alcohol (Ethanol) and *vice versa*.



(2) **Conversion of Acetic acid (Ethanoic acid) into Propionic acid (Propanoic acid) and *vice versa*.**

$$\begin{tikzcd}
\underset{\text{Acetic acid}}{CH_3COOH} \arrow[r, "\text{Heat Ca-salt} + \text{Ca-formate}"] & \underset{\text{Acetaldehyde}}{CH_3CHO} \arrow[r, "2H"] & \underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \arrow[r, "P+I_2"] & \underset{\text{Ethyl iodide}}{C_2H_5I} \arrow[d, "KCN"] \\
\underset{\text{Propionamide}}{C_2H_5CONH_2} \arrow[d, "Br_2+KOH"] & \underset{\text{Amm. propionate}}{C_2H_5COONH_4} \arrow[l, "\text{Heat}"'] & \underset{\text{Propiponic acid}}{C_2H_5COOH} \arrow[l, "NH_3"'] & \underset{\text{Ethyl cyanide}}{C_2H_5CN} \arrow[l, "H_2O"'] \\
\underset{\text{Ethylamine}}{C_2H_5NH_2} \arrow[r, "HONO"] & \underset{\text{Ethyl alcohol}}{C_2H_5OH} \arrow[r, "O"] & \underset{\text{Acetaldehyde}}{CH_3CHO} \arrow[r, "O"] & \underset{\text{Acetic acid}}{CH_3COOH}
\end{tikzcd}$$

(3) **Conversion of Ethylamine into Propylamine and *vice versa*.**

$$\begin{tikzcd}
\underset{\text{Ethylamine}}{C_2H_5NH_2} \arrow[r, "HONO"] & \underset{\text{Ethyl alcohol}}{C_2H_5OH} \arrow[r, "P+I_2"] & \underset{\text{Ethyl iodide}}{C_2H_5I} \arrow[r, "KCN"] & \underset{\text{Ethyl cyanide}}{C_2H_5CN} \arrow[d, "4H"] \\
\underset{\text{Propionic acid}}{C_2H_5COOH} \arrow[d, "NH_3"] & \underset{\text{Propionaldehyde}}{C_2H_5CHO} \arrow[l, "O"'] & \underset{\text{Propyl alcohol}}{C_2H_5CH_2OH} \arrow[l, "O"'] & \underset{\text{Propylamine}}{C_2H_5CH_2NH_2} \arrow[l, "HONO"'] \\
\underset{\text{Amm. propionate}}{C_2H_5COONH_4} \arrow[r, "\text{Heat}"] & \underset{\text{Propionamide}}{C_2H_5CONH_2} \arrow[r, "Br_2+KOH"] & \underset{\text{Ethylamine}}{C_2H_5NH_2} &
\end{tikzcd}$$

(4) **Conversion of Acetaldehdye (Ethanal) into Propionaldehyde (Propanal) and *vice versa*.**

$$\begin{tikzcd}
\underset{\text{Acetaldehyde}}{CH_3CHO} \arrow[r, "2H"] & \underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \arrow[r, "P+I_2"] & \underset{\text{Ethyl iodide}}{CH_3CH_2I} \arrow[r, "KCN"] & \underset{\text{Ethyl cyanide}}{CH_3CH_2CN} \arrow[d, "H_2O"] \\
\underset{\text{Propionaldehyde}}{CH_3CH_2.CHO} \arrow[d, "O"] & & \underset{\text{Propionic acid}}{CH_3CH_2COOH} \arrow[ll, "\text{Heat}"', "\text{Ca-salt} + \text{Ca-formate}"] & \underset{\text{propionamide}}{CH_3CH_2CONH_2} \arrow[l, "H_2O"'] \\
\underset{\text{Propionic acid}}{CH_3CH_2.COOH} \arrow[r, "NH_3"] & \underset{\text{Amm. propionate}}{CH_3CH_2.COONH_4} \arrow[rr, "\text{Heat}"] & & \underset{\text{propionamide}}{CH_3CH_2CONH_2} \arrow[d, "Br_2+KOH"] \\
\underset{\text{Acetaldehyde}}{CH_3CHO} & & \underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \arrow[ll, "O"'] & \underset{\text{Ethylamine}}{CH_3CH_2NH_2} \arrow[l, "HONO"']
\end{tikzcd}$$

(5) **Conversion of Methane into Ethane and *vice versa***

$$\begin{tikzcd}
\underset{\text{Methane}}{CH_4} \arrow[r, "Cl_2"] & \underset{\text{Methyl chloride}}{CH_3Cl} \arrow[r, "+2Na", "\text{Heat}"'] & \underset{\text{Ethane}}{C_2H_6} \arrow[r, "Cl_2"] & \underset{\text{Ethyl chloride}}{C_2H_5Cl} \arrow[d, "KOH\ (aq)"] \\
\underset{\text{Methane}}{CH_4} & \underset{\text{Acetic acid}}{CH_3COOH} \arrow[l, "\text{Soda lime}"', "\text{distil}"] & \underset{\text{Acetaldehyde}}{CH_3CHO} \arrow[l, "O"'] & \underset{\text{Ethyl alcohol}}{C_2H_5OH} \arrow[l, "O"']
\end{tikzcd}$$

4. **Conversion of unsaturated into less unsaturated or saturated hydrocarbons and *vice versa*** (*see* page *2·72*).

5. Ascent and Descent of series in Olefins and Acetylenes (*see* page 2·73).

6. Miscellaneous Conversions.—No chain reactions can be given for such conversions. Each particular conversion has a definite procedure based on the chemical reactions of various substances involved. A few examples are given below :

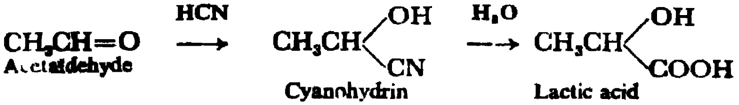
(1) Preparation of acetic acid from Acetylene.

$$\underset{\text{Acetylene}}{CH\equiv CH} \xrightarrow[HgSO_4]{42\%\ H_2SO_4+} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{O} \underset{\text{Acetic acid}}{CH_3COOH}$$

(2) Preparation of Methylamine from Acetic acid.

$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{NH_3} \underset{\text{Amm. acetate}}{CH_3COONH_4} \xrightarrow{\text{Heat}} \underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow{Br_2+KOH} \underset{\text{Methylamine}}{CH_3NH_2}$$

(3) Preparation of Lactic acid from Acetaldehyde.



$$\underset{\text{Acetaldehyde}}{CH_3CH=O} \xrightarrow{HCN} \underset{\text{Cyanohydrin}}{CH_3CH\langle^{OH}_{CN}} \xrightarrow{H_2O} \underset{\text{Lactic acid}}{CH_3CH\langle^{OH}_{COOH}}$$

(4) Conversion of a primary alcohol into secondary alcohol and *vice versa*.

$$\begin{tikzcd}
\underset{\text{Primary alcohol}}{RCH_2.CH_2OH} \arrow[r, "\substack{\text{Conc. } H_2SO_4 \\ 430K}", "-H_2O"'] & \underset{\text{Olefin}}{RCH=CH_2} \arrow[r, "HI", "\text{Addition}"'] & \underset{\text{Iodide}}{RCHI—CH_3} \arrow[d, "\text{KOH aq.}"] \\
\underset{\text{Alkyl bromide}}{RCH_2CH_2Br} \arrow[u, "\text{KOH aq.}"] & \underset{\text{Olefin}}{RCH=CH_2} \arrow[l, "HBr+"', "\text{Peroxide}"] & \underset{\text{Secondary alcohol}}{RCHOH.CH_3} \arrow[l, "H_2SO_4"', "-H_2O"]
\end{tikzcd}$$

(5) Conversion of Acetylene into Crotonaldehyde and *n*-butyl alcohol.

$$\underset{\text{Acetylene}}{CH\equiv CH} \xrightarrow[+HgSO_4\,;\ 330K]{42\%H_2SO_4} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[\text{alkali}]{\text{Dil}} \underset{\text{Aldol}}{CH_3CHOH.CH_2CHO}$$

$$\xrightarrow[-H_2O]{\text{Heat with } ZnCl_2} \underset{\text{Crotonaldehyde}}{CH_3CH=CH.CHO} \xrightarrow{H} \underset{n\text{-butyl alcohol}}{CH_3.CH_2.CH_2.CH_2OH}$$

(6) Conversion of Acetylene into Trichloroethylene.

$$\underset{\text{Acetylene}}{CH\equiv CH} \xrightarrow[\substack{Fe+ \\ \text{Kieselguhr}}]{Cl_2} \underset{\substack{\text{Acetylene} \\ \text{tetrachloride} \\ (\textit{Westron})}}{CHCl_2—CHCl_2} \xrightarrow[\text{Heated } BaCl_2]{\text{Passed over}} \underset{\substack{\text{Trichloroethylene} \\ (\textit{Westrosol})}}{CHCl=CCl_2} + HCl$$

(7) Conversion of Allyl iodide into Mustard oil.

$$\underset{\text{Allyl iodide}}{CH_2=CH—CH_2\boxed{I+K}CNS} \xrightarrow[-KI]{\text{Heat}} \underset{\text{Allyl thiocyanate}}{CH_2=CH.CH_2CNS}$$

$$\xrightarrow[\text{Isomerises}]{\text{Heat}} \underset{\substack{\text{Allyl isothiocyanate} \\ (\textit{Mustard oil})}}{CH_2=CH—CH_2—N=C=S}$$

QUESTIONS

1. **How will you convert :**
   (a) Acetaldehyde into propionaldehyde and *vice versa* ?
   (b) Methylamine into ethylamine and *vice versa* ?
   (c) Propylene into glycerol ? (*Delhi B.Sc. Hons. 1980*)
2. Giving equations and necessary conditions (if any), attempt any four of the following conversions :
   (i) Methylmagnesium iodide into acetic acid.
   (ii) Diethyl malonate into succinic acid.
   (iii) Diethyl malonate into barbituric acid.
   (iv) Methylmagnesium iodide into *tert.* butyl alcohol.
   (v) Ethyl acetoacetate into acetone. (*Delhi B.Sc. Hons. 1980*)
3. How will you convert—
   (i) Ethyl alcohol to chloroform.
   (ii) Acetone to *tert.* butyl alcohol.
   (iii) Acetaldehyde to α-hydroxyacetic acid.
   (iv) 1-Propanol to 2-Propanol. (*Delhi B.Sc. 1979*)
4. How will you carry out any *four* of the following conversions ?
   (a) 2-Chlorobutane to 3,4-dimethylhexane.
   (b) Propanamide to ethyl alcohol.
   (c) Acetylene to acetaldehyde.
   (d) *n*-propyl alcohol to isopropyl alcohol.
   (e) Propylene to glycerol.
   (f) Acetylene to propyne. (*Delhi B.Sc. 1980*)
5. Formulate the equations to show how the following conversions could be accomplished. Give the conditions necessary.
   (a) Phenol to salicylaldehyde.
   (b) Ethyl chloride to *n*-butane.
   (c) 1 : 1-dibromoethane to acetylene.
   (d) Ethyl alcohol to iodoform.
   (e) Acetaldehyde to lactic acid.
   (f) *n*-Butane to thiophen. (*Osmania B.Sc. 1979*)
6. Detail the steps for effecting any *four* of the following conversions :
   (i) Acetylene into acetone (ii) Acetyl chloride into acetaldehyde
   (iii) Ethyl alcohol into methane (iv) *n*-propyl alcohol into *t*-butyl alcohol
   (v) Methylamine into ethylamine (*Delhi B.Sc. 1981*)
7. How will you prepare—
   (a) Methylamine from acetic acid ?
   (b) Ethylamine from acetic acid ?
   (c) *n*-Butylamine from *n*-propyl bromide ?
   (d) *n*-Butylamine from *n*-pentyl bromide ? (*Agra B.Sc. 1978*)
8. How will you synthesize :
   (a) Iodoform from ethyl alcohol ?
   (b) 2-Butanol from acetylene ? (*Andhra B Sc. 1979*)
9. How will you synthesize from acetylene—
   (a) Ethanol, (b) Crotonic acid, (c) Vinyl chloride,
   (d) 2-Butyne ? (*Maharishi Dayanand B.Sc. 1979*)
10. How will you prepare—
    (a) Ethylamine from methyl alcohol.
    (b) 2-Methyl-2-butanol from acetone.
    (c) Lactic acid from acetaldehyde.
    (d) β-Hydroxypropionic acid from Ethylene.
    (*Maharishi Dayanand B.Sc. 1979*)

11. How will you synthesize the following from acetylene by using any needed organic or inorganic reagents :

(*a*) Butyne, (*b*) Acetaldehyde, (*c*) Vinyl chloride,
(*d*) Vinyl acetate. (*Guru Nanak Dev B.Sc. 1979*)

12. How will you convert

(*a*) Methane into acetic acid and *vice versa*.

(*b*) Ethyl alcohol into diethyl ether and *vice versa*.
(*Punjabi B.Sc. 1979*)

13. How will you convert *n*-propyl alcohol into isopropyl alcohol ?
(*Himachal B.Sc. 1979*)

14. How will you synthesize :

(*a*) Propionic acid from acetic acid ?

(*b*) 1,2,3-trihydroxypropane from propene ?
(*Sri Venkateswara B. Sc. 1979*)

15. How will you effect the following conversions :

(*i*) Acetic acid into acetamide (*ii*) Acetic acid into acetyl chloride.
(*iii*) Glycerol to formic acid (*iv*) Oxalic acid to formic acid
(*v*) Ethane into ethylene glycol (*vi*) Ethanol to ethene
(*vii*) Urea to malonylurea (*viii*) Ethyne to copper ethynide.
(*Delhi B.Sc. Hons. Sub. 1982*)

16. How will you bring about the following conversions :

(*a*) β-Hydroxy propionic acid from ethylene.
(*b*) Lactic acid from acetaldehyde.
(*c*) α-Aminopropionic acid from acetaldehyde.
(*d*) Nitromethane from acetic acid.
(*e*) Methyl cyanide from acetaldehyde.
(*f*) Ethylamine from propionamide ? (*Meerut B.Sc., 1980*)

17. How will you obtain the following :

(*a*) Formic acid from glycerol,
(*b*) Acetaldehyde from acetylene,
(*c*) Tertiary alcohols using Grignard's reagent,
(*d*) Isocyanide from primary amines ? (*Delhi B.Sc. Hons., 1982*)

18. How can the following conversions be done :

(*i*) CH_3CHO to $CH_3CH(OH)COOH$
(*ii*) $CH{\equiv}CH$ to $CH_2{=}CH{-}C(Cl){=}CH_2$
(*iii*) $CH_3{-}CH{=}CH{-}CH_3$ to CH_3CHO
(*iv*) $CH_3CH_2CH_2OH$ to $CH_3CH(OH)CH_3$? (*Delhi B.Sc. 1982*)

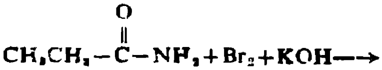
Appendix 3

MISCELLANEOUS QUESTIONS

(A) WHAT HAPPENS

1. Predict the compound formed in each of the following reactions ;
   - (*i*) $CH_3CH_2CH{=}CH_2 + HBr \longrightarrow$
   - (*ii*) $CH_3CHO + CH_3MgBr \longrightarrow A \xrightarrow{\text{Hydrolysed}} B$
   - (*iii*) $C_2H_5OC_2H_5 + HI \xrightarrow{\text{in cold}}$
   - (*iv*) $CH_2OH-CHOH-CH_2OH \xrightarrow{KHSO_4}$

(*Delhi B.Sc. Hons. Sub. 1982*)

2. Complete the following reaction equations :
   - (*a*) $R-C{\equiv}CH \xrightarrow{H_2SO_4/HgSO_4}$
   - (*b*) $CH_3COOH \xrightarrow{LiAlH_4}$
   - (*c*) 
     $CH_3CH_2-\overset{\overset{\Large O}{\|}}{C}-NH_2 + Br_2 + KOH \longrightarrow$
   - (*d*) $CH_3CO.CH_2COOEt + H_2N.CO.NH_2 \longrightarrow$
   - (*e*) $HCHO + NH_3 \longrightarrow$

(*Delhi B Sc. Hons. Sub. 1982*)

3. What happens when :
   - (*i*) Urea is treated with HNO_2.
   - (*ii*) C_2H_5MgBr is treated with acetamide.
   - (*iii*) β-Hydroxypropionic acid is treated with HI.
   - (*iv*) Ethylamine is heated with CS_2 in presence of $HgCl_2$?

(*Agra B.Sc. 1980*)

4. What happens when :
   - (*i*) Nitric acid reacts with glycerol.
   - (*ii*) Ethamol is distilled with bleaching powder.
   - (*iii*) Citric acid is heated with fuming sulphuric acid.
   - (*iv*) Acetylene is passed through red hot tube.
   - (*v*) Glycerol is heated with oxalic acid at 260°C.
   - (*vi*) Acetylene is passed into acetic acid. (*Kanpur B.Sc. 1980*)
5. What happens when :
   - (*a*) Glycine is heated.
   - (*b*) Acetamide reacts with Br_2 and KOH.
   - (*c*) Citric acid reacts with fuming sulphuric acid.
   - (*d*) Urea is treated with malonic ester. (*Jiwaji B.Sc. 1980*)
6. What happens when—
   - (*a*) *tert*. Butyl alcohol vapours are passed over heated copper at 300°C.
   - (*b*) Isopropyl alcohol is oxidised with $K_2Cr_2O_7$ and H_2SO_4.
   - (*c*) 2-Butanol is treated with conc.H_2SO_4.
   - (*d*) Cyclopropane is treated with HI.
   - (*e*) 2-Butene is treated with diazomethane in presence of light.

(*Guru Nanak Dev. B.Sc. 1982*)

7. **What happens when—**
   (*i*) 2, 2-dimethylpropanal reacts with NaOH ?
   (*ii*) Glycerol reacts with HI ?
   (*iii*) Acetone is reduced with magnesium amalgam ?
   (*iv*) Acetamide reacts with bromine and caustic potash ?
   (*Delhi B.Sc. Hons. 1980*)

8. **What happens when—**
   (*i*) acetamide is treated with bromine and alcoholic potash,
   (*ii*) methylmalonic acid is heated,
   (*iii*) urea is heated,
   (*iv*) ethylmagnesium iodide is treated with CO_2 and the product hydrolysed with acid,
   (*v*) methyl cyanide is boiled with NaOH,
   (*vi*) citric acid is heated with fuming sulphuric acid,
   (*vii*) ethyl acetoacetate is treated with urea ?
   (*Delhi B.Sc. 1979*)

9. Complete the following reactions :
   (*a*) $CH_3CH=CH_2 \xrightarrow{Cl_2,\ 770\ K}$
   (*b*) $CH_3CH=CHCH_3 \xrightarrow{Al_2(SO_4)_3,\ Heat}$
   (*c*) $CH_3CH_2CH=CH_2 \xrightarrow{O_3/ether} A \xrightarrow{H_2/Pt} B$
   (*d*) $(CH_3)_2C=CH_2+H_2O \xrightarrow{H+}$
   (*Aligarh B.Sc. 1979 Supp.*)

10. Write the products for the following reactions (give formula only) :
   (*i*) Acetaldehyde + Methylmagnesium iodide followed by hydrolysis.
   (*ii*) Benzoyl chloride + hydrogen in presence of palladium.
   (*iii*) Formaldehyde + aq. NaOH. (*Osmania B.Sc. 1979*)

11. Complete the following reactions :
   (*a*) $CH_3COOH \xrightarrow{LiAlH_4}$
   (*b*) $CH_3CH_2CH_2COOH \xrightarrow{PCl_5}$
   (*c*) $CH_3CH_2NH_2+CHCl_3+KOH \xrightarrow{C_2H_5OH\ \ Heat}$
   (*d*) $(HCOO)_2Ca \xrightarrow{Heat}$
   (*e*) $NH_2—CO-NH_2+HNO_2 \longrightarrow$
   (*f*) $CH_3CONH_2 \xrightarrow{P_4O_{10}}$
   (*g*) $CH_3COOH+C_2H_5OH \xrightarrow{H+}$
   (*h*) $CH_3C\equiv N+H_2O \xrightarrow{H+}$ (*Delhi B.Sc. 1980*)

12. Describe any *four* giving equations, what happens when—
   (*i*) Glycerol reacts with oxalic acid.
   (*ii*) Glycerol reacts with hydrogen iodide.
   (*iii*) Diethyl ether reacts with hydrogen iodide.
   (*iv*) Chloroform is treated with phenol in the presence of alcoholic potash.
   (*v*) Chloroform is treated with a primary amine in the presence of alcoholic potash.
   (*vi*) Sodium salt of phenol reacts with CO_2 and the product is acidified. (*Delhi B.Sc. Hons. Sub. 1980*)

13. Write equations for the following reactions. Give the mechanism in each case.

(*a*) Isoprene is treated with 30% HBr in acetic acid.

(*b*) Isopropyl bromide is treated separately with aqueous NaOH and alcoholic NaOH.

(*c*) Equimolecular quantities of a mixture of isobutane and chlorine are exposed to sunlight.

(*d*) *n*-Butane is heated with fuming HNO_3 in vapour phase.

((*Delhi B.Sc. Hons. 1981*)

14. Give the mechanism of the reactions in the following cases :

(*i*) Propylene is treated with HBr in absence of peroxides.

(*ii*) Ethyl bromide is treated with equeous KOH. (*Delhi B.Sc. 1981*)

15. Complete the following reactions :

(*i*) $CH_3COCl \xrightarrow{LiAlH_4}$

(*ii*) $CH_3.CH(OH).CH_3 \xrightarrow{Cu,\ 300°C}$

(*iii*) $CH_2OH—CH_2OH \xrightarrow{\text{anhy } Z_nCl_2}$

(*iv*) $CH_3COCH_3 \xrightarrow{PCl_5}$

(*v*) $CH_3CH_2Br \xrightarrow{AgNO_2}$

(*vi*) $CH_3CH{=}CH_2 \xrightarrow{Cl_2,\ 500°C}$

(*vii*) $CH_3CH(OH).CH_2OH \xrightarrow{Pb(OAc)_4}$ (*Delhi B.Sc. 1982*)

(B) STRUCTURAL FORMULA

1. Give the structural formulae of any six of the following :

(*i*) Freon (*ii*) Carbinol (*iii*) Mustard gas

(*iv*) Allylene (*v*) Dimethyl glyoxime (*vi*) Crotonic acid

(*vii*) Vinyl bromide. (*Kanpur B.Sc. 1980*)

2. Give the structure of :

(*a*) Mustard gas (*b*) Lewisite (*c*) Freon-12

(*d*) Chloretone (*e*) Westrosol (*Kanpur B.Sc. 1979*)

3. Give the structural formulae of :

(*a*) (*i*) 2-Hydroxylbutane, (*ii*) 1-Bromo-2-chlorobutane, (*iii*) *n*-Propylmagnesium iodide.

(*b*) (*i*) Ethyl acetoacetate, (*ii*) Acetone dicarboxylic acid, (*iii*) Fumaric acid ; (*iv*) Isobutyric acid. (*Delhi B.Sc. 1970*)

(C) NAME REACTIONS

1. Write short notes on :

(*i*) Wurtz Reaction. (*Delhi B.Sc. 1979*)

(*ii*) Cannizzaro's Reaction. (*Delhi B.Sc. 1979*)

(*iii*) Hofmann Bromamide Reaction or Hofmann Degradation. (*Delhi B.Sc. 1972*)

(*iv*) Clemmensen reduction.

(*v*) Gabriel's Phthalimide Synthesis.

(*vi*) Hofmann Mustard Oil Reaction.

(*vii*) Meerwein-Ponndorf-Verley Reduction.

(*viii*) Knoevenagel Reaction.

(*ix*) Oppenauer Oxidation.

(*x*) Wolff-Kishner Reduction.

(*xi*) Hell Volhard-Zelinsky Reaction.

(*xii*) Claisen condensation.

(*xiii*) Stephen's Reaction.

(*xiv*) Mendius Reaction.

(*xv*) Arndt-Eistert Synthesis.

2. What important things in Chemistry are associated with the names of (*i*) Fischer-Tropsch, (*ii*) Frankland, (*iii*) Clemmensen, (*iv*) Markownikoff, (*v*) Victor Meyer, (*vi*) Baeyer, and (*vii*) Kolbe.

(D) OTHER REACTIONS

1. Write short notes on :

(*i*) Aldol condensation. (*Saugor B.Sc. 1979 ; Lucknow 1978*)

(*ii*) Biuret Test.

(*iii*) Haloform Reaction or Iodoform Reaction.

(E) IMPORTANT REAGENTS

1. What are the reagents named after Baeyer, Schiff and Tollens and what is their importance in Organic Chemistry ?

2. (*a*) For what purpose are the following substances used in Organic Chemistry : (*i*) Zinc-copper couple ; (*ii*) Sodium amalgam ; (*iii*) Anhydrous aluminium chloride ; and (*iv*) Hydroxylamine ?

(*b*) Write a short note on the use of sodium in organic synthesis.

3. Illustrate by examples the application of any three of the following (*a*) Phosgene, (*b*) phenylhydrazine, and (*c*) acetic anhydride.

4. Discuss the use of the following reagents in inorganic chemistry giving suitable examples :

(*i*) Fehling's solution ; (*ii*) Iodine solution ; and

(*iii*) Phosphorus pentachloride.

(F) HOW WILL YOU DISTINGUISH BETWEEN

1. (*a*) 1-Butyne and 2-Butyne.

(*b*) Acetone and Acetaldehyde.

(*c*) Acetic acid and Formic acid.

(*d*) 1-Propanol and 2-Propanol.

(*e*) Isopropyl alcohol and *n*-Propyl alcohol.

(*f*) Ethyl alcohol and Diethyl ether.

(*Calcutta B.Sc. 1977 ; Andhra 1978 ; Udaipur 1978 ; Kerala 1977 ; Shivaji 1977*)

2. (*a*) Ethyl alcohol and Dimethyl ether.

(*b*) Nitroethane and ethyl nitrite. (*Madurai B.Sc. 1977*)

(*c*) Propane and Propene. (*Agra B.Sc. 1977*)

3. (*a*) Methanol and Ethanol .

(*b*) Ethanol and Acetylene.

(*Punjab B.Sc. 1977 ; Udaipur 1978 ; Burdwan 1978*)

4. (*a*) Ethylamine and Diethylamine.

(*b*) Nitroethane and Ethyl nitrite.

(*c*) *n*-Butyl alcohol and Diethyl ether. (*Rajasthan B.Sc. 1977*)

5. (*a*) Vinyl bromide and allyl bromide

(*b*) 1,3-Butadiene and *n*-Butane.

(*c*) *tert*. butyl alcohol and *n*-Butyl alcohol. (*Meerut B.Sc. 1978*)

6. (*a*) Ethylene and acetylene.

(*b*) *n* Butyl alcohol and Diethyl ether. (*Osmania B.Sc. 1978*)

7. (*i*) Alkylnitrites and nitroalkanes.

(*ii*) Vegetable oil and mineral oil ;

(*iii*) Tartaric acid and citric acid

(*iv*) Dimethylamine and ethylamine. (*Agra B.Sc. 1980*)

8. How will you distinguish between :

(*a*) Acetone, ethanol and dimethyl ether ?

(*b*) Ethyl methyl ketone and diethyl ketone ?

(*c*) Diethyl ether and ethyl acetate ?

(*d*) Allyl chloride and vinyl chloride ? (*Delhi B.Sc. 1981*)

(G) HOW WILL YOU PREPARE

1. How will you prepare any four of the following :

(*a*) Ethyl methyl ketone ; (*b*) Malic acid ; (*c*) Ethylmagnesium bromide ; (*d*) Freon ; (*e*) Trichloromethane ; (*f*) Westrosol.

2. How will you prepare any four of the following :

(*a*) Ethyl mercaptan ; (*b*) Acetal ; (*c*) Acetic anhydride ; (*d*) Cyanoacetic acid ; (*e*) β-Chloroethyl alcohol ; (*f*) Monochloroacetic acid.

3. How will you prepare any five of the following :

(*a*) Vinegar ; (*b*) Oxalic acid ; (*c*) Biuret ; (*d*) Allyl alcohol ; (*e*) Mustard gas ; (*f*) Ethyl cyanoacetate ; (*g*) Hydracrylic acid ; (*h*) Methylene iodide ; (*i*) Acrolein.

4. Starting from malonic ester, how will you prepare :

(*i*) Barbituric acid, (*ii*) Succinic acid, (*iii*) Dimethylacetic acid,
(*iv*) Methyl ethyl ketone ? (*Delhi B.Sc. 1971*)

5. Describe, giving equations, the preparation of the following : Formic acid, sulphonal, Diethylamine, Tetraethyl-lead. (*Delhi B.Sc. 1972*)

6. Describe, giving equations, the preparation of the following :

Lewisite. Isoprene, Succinic acid from ethyl alcohol and Diethyl malonate from acetic acid. (*Delhi B.Sc. 1971*)

7. How would you prepare the following :

(*i*) Propyne from ethyne ;

(*ii*) β, β′ Di-chloro-diethyl sulphide from ethylene

(*iii*) Acrylic acid from allyl alcohol ?

(H) HOW WILL YOU SHOW

1. How will you show that

(*a*) Citric acid is a β-hydroxy acid.

(*b*) In propane there are two carbon atoms on one side and one carbon atom on the other side of the double bond.

(*c*) Alkyl cyanides are not true esters.

(*d*) A double bond is essential for geometrical isomerism.

(*e*) Tautomerism differs from resonance effect.

2. How will you show that

(*a*) Homologues can never be isomers.

(*b*) In ethylene bromide, the two bromine atoms are attached to different carbon atoms.

(*c*) In chloral the chlorine atoms are linked to only one carbon atom.

3. How will you show that :

(*a*) In glycol the —OH groups are linked to different carbon atoms.

(*b*) Glycerol has three hydroxyl groups.

(*c*) In acetaldehyde the two carbon atoms are directly linked.

4. How will you show that :

(*a*) In nitromethane the nitrogen and carbon atoms are directly linked.

(*b*) In urea the carbon atom is directly linked to both the nitrogen atoms.

(*c*) In methyl cyanide the nitrogen atom is directly linked to only one carbon atom.

5. How will you show that :

(*a*) Lactic acid is an α-hydroxy acid and a derivative of propionic acid.

(*b*) Acetoacetic ester is a β-keto as well as unsaturated hydroxy compound.

(c) Optical activity of a molecule is linked with the presence of chiral carbon atom.

(F) EXPLAIN WHY

1. (*i*) Addition of hydrobromic acid to propene in the presence of a peroxide is against Markownikoff's rule.

(*ii*) Hydrogen atoms of malonic ester are reactive. (*Delhi B.Sc. 1971*)

2. (*a*) Conjugated dienes are more stable than isolated dienes.

(*b*) Four C—H bonds in methane are equivalent.

(*c*) Acetylene is acidic in nature.

(*d*) Methylamine is more basic than ammonia.
(*Visva Bharti B.Sc. 1978 ; Andhra 1978 ; Kurukshtra 1979 ; Agra 1979*)

3. (*a*) Ethyl alcohol is soluble in water but dimethyl ether is not, though they have the same molecular formula.

(*b*) Ethylamine is basic while acetamide is not. (*Udaipur B.Sc. 1978*)

4. (*a*) Alcohols are high boiling liquids as compared to alkanes.

(*b*) Chloroacetic acid is stronger acid than acetic acid.

(*c*) Methylamine is more basic than ammonia.
(*Bombay B.Sc. 1978 Andhra 1979 ; Delhi 1979*)

5. (*a*) Vinyl bromide is less reactive than ethyl bromide.

(*b*) Formic acid is stronger than acetic acid. (*Punjabi B.Sc. 1979*)

6. (*i*) Water has higher boiling point than ethyl alcohol.

(*ii*) $(CH_3)_3$ N is soluble in water but $(CH_3)_3CH$ is not.

(*iii*) A carboxylic acid does not form an oxime with NH_2OH

(*iv*) Ethane is insoluble in water while ethyl alcohol is soluble in it.

(*v*) Acetic acid is stronger than propionic acid but weaker than monochloroacetic acid. (*Agra B.Sc. 1979, 77*)

7, (*i*) Acrylic acid is a stronger acid than acetic acid.

(*ii*) Meso compounds are optically inactive.

(*iii*) Glycine behaves both as an acid and a base.

(*iv*) Maleic acid froms an anhydride while fumaric acid does not.

(*v*) Urethan is prepared by the reaction of isocyanate and absolute alcohol. (*Delhi B.Sc. 1978*)

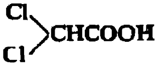
8. "All amines are stronger bases than ammonia", Discuss the statement and compare the basic strength of the following giving reasons :

(*a*) Ammonia, (*b*) Methylamine, (*c*) Dimethylamine,
(*d*) Trimethylamine. (*Gorakhpur B.Sc. 1977*)

9. (*a*) During esterification, it is the O—H bond in alcohols that breaks.

(*b*) Arrange the following acids according to their increasing acid strength, giving reasons :

(*i*) HCOOH, (*ii*) CH_3COOH, (*iii*) $ClCH_2COOH$,

(*iv*)

$\mathrm{Cl_2CHCOOH}$

(*c*) Why are primary amines more basic than ammonia ?
(*Delhi B.Sc. Hons. 1982*)

(J) SHORT NOTES

1. Write short notes on :

(*a*) (*i*) Polymerisation (*ii*) Petrochemicals
(*iii*) Cracking. (*M.S. Baroda B.Sc 1978*)

(*b*) (*i*) Markownikoff's rule (*ii*) Geometric isomers
(*iii*) Absolute alcohol (*Osmania B.Sc. 1978*)

(*c*) (*i*) Synthetic detergents (*ii*) Cleansing action of soap.
(*Bombay B,Sc. 1978*)

(*d*) Baeyer's strain theory. (*Jammu B.Sc. 1978*)

(*e*) (*i*) Synthetic petrol. (*ii*) Fermentation.
(*Guru Nanak Dev B.Sc. 1979*)

(*f*) Strainless rings (*Maharishi Dayanand B.Sc. 1979*)

2. Write short notes on any four of the following :

(*i*) Condensation.
(*ii*) Enantiomorphs.
(*iii*) Saponification.
(*iv*) Esterification.
(*v*) Hydrolysis.
(*vi*) Hydrogenation.
(*vii*) Hydrogenation of Oils or Hardening of Oils.
(*viii*) Unsaturation.
(*x*) Ozonolysis.

3. Write short notes on the following :

(*i*) Geometrical isomerism. (*ii*) Cracking and its applications.
(*iii*) Reactive methylene group. (*Delhi B.Sc. 1972*)

(K) REACTION MECHANISMS

1. Explain with examples the difference in mechanism of reaction of C=C and C=O. (*Agra B.Sc. 1978*)

2. Explain the electronic mechanism of the following reactions :

(*a*) Aldol condensation, (*b*) Hydrolysis of primary alkyl halide with an alkali. (*Kanpur B.Sc. 1978*)

3. Discuss the mechanisms of the following reactions :

(*a*) 1 : 4-addition of Br_2 to 1 : 3-butadiene.

(*b*) Alkylation of alkene.

(*c*) Allylic substitution of propene.

(*d*) Dehydration of alcohol to form ether.

(*e*) Hydration of propene. (*Guru Nanak Dev B.Sc. 1982*)

4. (*a*) Why is isopropyl bromide obtained on reaction of HBr with propylene ?

(*b*) What happens to the above reaction on addition of peroxides ?

(*c*) Explain the mechanism of pinacol-pinacolone rearrangement.

(*d*) Explain the mechanism of Hofmann bromamide reaction. (*Delhi B.Sc. Hons. 1982*)

5. Give mechanisms for the following :

(*i*) Halogenation alkanes.

(*ii*) Electrophilic addition to olefinic bond.

(*iii*) Dehydration of alcohols.

(*iv*) Hydrolysis of esters in acidic medium. (*Delhi B.Sc. 1982*)

6. Discuss the mechanism of each of the following reactions :

(*a*) Reaction of NaOH with methyl chloride. (*Udaipur B.Sc. 1978 ; Delhi 1979*)

(*b*) Electrophilic addition to alkenes (*Guru Nanak Dev B.Sc. 1979*)

(*c*) Addition of halogen to carbon-carbon double bond. (*Udaipur B.Sc. 1979*)

Appendix 4

NEW TYPE QUESTION BANK—(II)

SHORT ANSWER TYPE :

1. Write various steps involved in the chlorination of methane.

2. Explain the following statements :

(*i*) Chlorination of alkanes is an exothermic reaction and yet it requires high temperature or exposure to high energy UV radiations for its success.

(*ii*) A more stable alkyl radical is formed more easily.

(*iii*) Halogenation in the presence of tetramethyl lead proceeds at low temperature than when it is done in its absence.

(*iv*) Iodination of methane does not take place, even when bromination and chlorination take place, in spite of the fact that iodine-iodine bond in the iodine molecule is the weakest. (*Guru Nanak Dev B.Sc. 1976*)

3. Explain why—

(*i*) Halogenation of the paraffins is an oxidative process.

(*ii*) A tertiary carbon atom can be oxidised with relative ease.

(*iii*) Why would one not prepare a Grignard reagent from $BrCH_2.CH_2OH$?

4. Write structural formulae for the following :

(*i*) 2, 2-Dimethylbutane. (*ii*) 4-Ethyl-2, 4-dimethylheptane.

(*iii*) *neo*-Hexane. (*iv*) 3, 4, 4-Trimethylheptane.

(*v*) 5-ethyl-2, 3-dimethyloctane.

5. Name the following alkanes :

(*i*) $(C_2H_5)_2CH.CH_3$; (*ii*) $(CH_3.CH_2.CH_2)_4C$; (*iii*) $(CH_3)_4C$

6. Which of the following reagents will react with *n*-butane ?

(*i*) Alkaline $KMnO_4$ solution. (*ii*) Aqueous KOH solution

(*iii*) Cold dilute nitric acid. (*iv*) Metallic sodium.

(*v*) Iodine in presence of light. (*vi*) Bromine in the dark.

(*vii*) Bromine in the presence of light. (*viii*) Chlorine in the dark.

(*ix*) Chlorine in the presence of light.

7. Why would the chlorination of ethane to ethyl chloride be a more practical synthesis than the chlorination of pentane to 1-chloropentane ?

8. An alkane with mol. wt. = 72 formed only one monochloro substitution product. Suggest a structure for the alkane.

9. What products are obtained when propane undergoes mono-substitution ? (*Delhi B.Sc Hons. Sub. 1977*)

10. Chlorination reactions of certain higher alkanes can be used for laboratory preparation, *e.g.*, for the preparation of neopentyl chloride from neopentane and cyclopentyl chloride from cyclopentane. What structural features of these compounds make this possible ?

11. Can isobutane be prepared by Wurtz reaction ?

12. Which higher homologue of methane is likely to be formed during its halogenation ?

13. Of the three isomeric pentanes, which one is expected to yield the largest number of isomeric monochloro derivatives ?

14. How would you obtain *n*-butane from (*i*) sec-butyl bromide, (*ii*) ethyl chloride, and (*iii*) But-1-ene ?

15. Write various possible structural formulae of alkanes with molecular formula C_6H_{14} and write IUPAC names.

16. *The greater the number of alkyl groups attached to the doubly bonded carbon atoms, the more stable the alkene.* Give the name of this rule and with its help arrange the following alkenes in the order of (*a*) Decreasing stability, and (*b*) decreasing ease of formation.

$R_2C=CR_2$; $R_2C=CH_2$; $CH_2=CH_2$; $R_2C=CHR$; $RCH=CHR$; $RCH=CH_2$.

17. Give structures of various alkenes expected from dehydrohalogenation of (*a*) 1-chloropentene ; (*b*) 2-chloropentene ; (*c*) 3-chloropentene ; (*d*) 2-chloro-2-methylybutane ; (*e*) 3-chloro-2-methylbutane ; (*f*) 2-chloro-2, 3-dimethylbutane ; (*g*) 1-chloro-2, 2-dimethylpropane. Predict the major product in each case.

18. What alkyl halide, if any, would yield each one of pure alkene upon dehydrohalogenation ?

(*a*) Isobutylene ; (*b*) 1-pentene ; (*c*) 2-pentene ; (*d*) 2-methyl-1-butene (*e*) 2-methyl-2-butene.

19. Predict the major product of dehydration of each of the following :

(*a*) $(CH_3)_2C(OH).CH_2.CH_3$; (*b*) $(CH_3)_2.CH.CHOH.CH_3$;

(*c*) $(CH_3)_2C(OH).CH(CH_3)_2$; (*d*) $CH_3.CH_2.CH_2.CH_2OH$.

20. (*a*) *Electrophilic addition to a carbon-carbon double bond involves the intermediate formation of the more stable carbocation.* Which rule is replaced by this general rule ?

(*b*) Addition of HCl to 3-methyl-1-butene yields mixture of two alkyl-chlorides. What are they likely to be and how is each formed ?

21. Free radical addition to a carbon-carbon double bond involves the intermediate formation of the more stable free radical. The stability of free radicals is in the order :

allyl > tertiary > secondary > primary > $CH_3^{\cdot}$ > vinyl

Keeping these facts in mind

(*a*) formulate the addition of Br_2 to propylene and addition of HBr to the resulting free radical, and

(*b*) explain the action of Cl_2 on propylene 770-870K

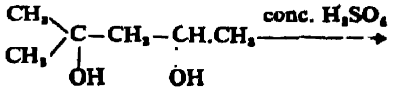
22. Complete the following reactions :

(*a*) $CH_3CH_2.CH=CH_2+HCl\longrightarrow$

(*b*) $(CH_3)_3CH+(CH_3)_2C=CH_2\xrightarrow{\text{Cold conc. } H_2SO_4}$

(*c*) $CH_3.CH=CH_2+HOCl\longrightarrow$

(*d*)



$$(CH_3)_2C(OH)-CH_2-CH(OH).CH_3\xrightarrow{\text{conc. } H_2SO_4}$$

(*e*) $(CH_3)_2C=CH_2\xrightarrow{\text{conc. } H_2SO_4}$

23. How you will prepare the following :

(*a*) Propane from *n*-propyl alcohol.

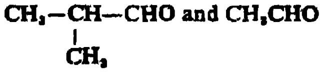
(*b*) *n*-Propyl bromide from propene.

(*c*) 1-Butene from 1, 2-dichlorobutane.

(*d*) Allyl chloride from propene. (*e*) Glycol from ethylene.

24. Give the structure of alkenes that yield on ozonolysis

(*i*) only acetone

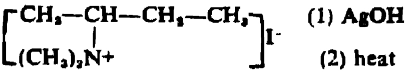
(*ii*) 

$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CHO$ and CH_3CHO

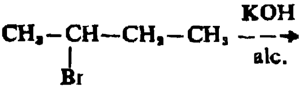
What would each of these alkenes yield upon cleavage by $KMnO_4$?

(*Punjab B.Sc. 1976 Suppl.*)

25. Complete the following reactions. Giving reasons in support of your answer, assign the structure to the main product formed in each case :

(*i*) 

$\left[CH_3-\underset{\displaystyle (CH_3)_3N^+}{\underset{|}{CH}}-CH_2-CH_3\right]I^- \quad \begin{array}{l}(1)\ AgOH\\(2)\ heat\end{array}$

(*ii*) 

$CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_2-CH_3 \xrightarrow[\text{alc.}]{KOH}$

(*iii*) $(CH_3)_3C-CH_2Br \xrightarrow{KOH}$ (*Delhi B.Sc. Hons. 1976*)

26. State and illustrate the rule which governs the addition of HBr to propylene. (*Delhi B.Sc. 1976*)

27. Account for the fact · Addition of bromine to ethylene in the presence of NaCl gives not only $BrCH_2.CH_2Br$ but also $BrCH_2.CH_2Cl$.

(*Kerala B.Sc. 1975*)

28. Explain briefly why butadiene gives 1,2 and 1,4 addition products.

(*Delhi B.Sc. Hons. 1976 ; B.Sc. 1977*)

29. Why is the chair form of cyclohexane more stable than the boat form ? Make diagrams of both forms. (*Delhi B.Sc. Hons. 1976*)

30. Write a note on mechanism of addition of bromine to ethylene.

(*Delhi B.Sc. 1977*)

31. Predict the products formed :

(*i*) $CH_3.CH_2.CH_2.CH_2OH \xrightarrow[\Delta\ (410K)]{\text{conc } H_2SO_4}$

(*ii*) $CH_3.CH{=}CH_2 \xrightarrow{HOCl}$ (*Delhi B.Sc. Hons. Sub. 1977*)

32. Name the following :

(*a*) $(CH_3)_2\ C{=}CH_2$. (*b*) $(CH_3)_2\ C{=}CHC_2H_5$.

(*c*) $CH_3.CH{=}CH.CH_3$. (*d*) $(CH_3)_2\ CH.CH{=}CH.CH_3$.

33. Write structural formulae for :

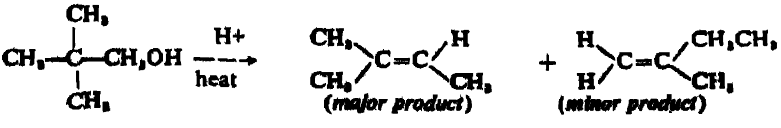
(*a*) 4-ethyl-5-methyl-2-hexene, (*b*) 2, 3-diethyl-1, 3-butadiene,

(*c*) Trimethylethylene or 2-Methylbut-2-ene,

(*d*) 3, 5-octadiene. (*e*) 3-methyl-1-butene,

34. Which compound would you expect to have large heat of hydrogenation (in kJ mol^{-1}) *cis*-cyclooctene or *trans*-cyclooctene ?

35. Write step-by-step mechanisms that account for each product of the following reactions and explain the relative proportions of the isomers obtained.

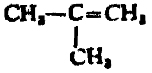


36. Show all steps in the acid-catalysed hydration of propene. Explain why the product is 2-propanol and not 1-propanol.

37. Give the structure and name of the product obtained on addition of HCl to propene.

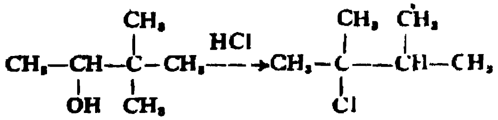
38. Write all steps of mechanism for the acid catalysed dimerisation of propene. What would be the major product ?

39. Arrange the following alkenes in order of reactivity towards acid-catalysed hydration and explain reasoning.



$$CH_2{=}CH_2,\quad CH_3{-}CH{=}CH_2,\quad CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2$$

40. Write a mechanism that explains the course of the following reaction :



$$CH_3{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}{-}CH_3 \xrightarrow{HCl} CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle Cl}{\underset{|}{C}}}}{-}\overset{\displaystyle CH_3}{\overset{|}{CH}}{-}CH_3$$

41. The relative rates of addition of hydrogen chloride to the following alkenes increase in the order below :

Ethene > propene > 2-Butene > 2-Methylpropene

Explain.

42. Explain the following equations :

(*i*) $CH_3{-}CH{=}CH_2 \xrightarrow[770\text{ K}]{Cl_2}$

(*ii*) $CH_3CHCl\,CH_2CH_3 \xrightarrow[EtOH]{OH^-}$

(*Delhi B.Sc. Hons Sub. 1978*)

43. Discuss the mechanism of addition of HBr to propene. (*Andhra B.Sc. 1978*)

44. Discuss the mechanism of free radical addition to conjugated dienes. (*Punjab B.Sc. 1971*)

45. When HBr is added to propylene in presence of peroxides, what is the compound that is formed ? (*Kamraj B.Sc. 1981*)

46. Draw the tetrahedral shape of methane molecule. (*Kamraj B.Sc. 1981*)

47. What is the difference between a nucleophilic and an electrophilic reagent ? (*Kamraj B.Sc. 1981*)

48. Explain homolytic fission and heterolytic fission of C-C bonds (*Kamraj B.Sc. 1981*)

49. How is Westron obtained from acetylene ? State its use. (*Kamraj B.Sc. 1981*)

50. Acetylene is acidic while ethylene is not. Explain why. (*Kamraj B.Sc. 1981*)

51. CH_3CH_2I is more reactive than CH_3CH_2Cl towards KCN. Explain why. (*Kamraj B.Sc. 1981*)

52. Formic acid is a stronger acid than acetic acid. Explain. (*Kamraj B.Sc. 1981*)

53. Draw the structure of the simplest hydrocarbon containing a tertiary carbon atom. (*Kamraj B.Sc. 1981*)

54. $$HC\equiv CH \xrightarrow{HX} A \xrightarrow{HX} B$$
What is the final produce in the above sequence of operations. ?
(*Kanauj B Sc. 1981*)

55. Explain why acetylene is acidic in nature. (*Delhi B.Sc. 1977*)

56. How are the following pairs distinguished ? Give one reaction.

$CH_3.CH_2.C\equiv CH$ and $CH_3.C=C.CH_3$

(*Delhi B.Sc. Hons. Sub. 1977*)

57. What happens when acetylene is passed through warm acetic acid in the presence of mercuric ions ? (*Delhi B.Sc. Hons. 1977*)

58. Write and draw an orbital structure of acetylene.
(*Guru Nanak Dev B.Sc. 1977*)

59. Give two properties each of electrophilic and nucleophilic additions on acetylene along with their mechanisms. (*Guru Nanak Dev B.Sc. 1977*)

60. Account for the fact—Acetylene forms a sodium derivative but ethylene does not. (*Madras B.Sc. 1976 September*)

61. Give the shapes and bond angles of (*i*) ethylene and (*ii*) acetylene. Mention the state of hybridisation of carbon in these compounds.
(*Osmania B Sc. 1975*)

62. How are alkynes distinguished from alkenes.
(*Marathwada B.Sc. 1976*)

63. Write the structural formulae for :

(*a*) 4-Methyl-2-pentyne ; (*b*) Diethylacetylene ;

(*c*) Dimetylacetylene ; (*d*) 3, 4, 4-Trimethyl-1-pentyne.

Give IUPAC names of (*b*) and (*c*).

Which of these compounds give a positive test with $Ag(NH_3)_2^+OH^-$?

64. Give the structure of the products obtained when 1-pentyne reacts with :

(*a*) one mole of Br_2 (*b*) one mole of HCl

(*c*) two moles of HCl (*d*) one mole of HBr and a peroxide.

65. Write structural formulae for :

(*i*) 2-Chloro-3-Methylbutane. (*ii*) 1, 3-Di-iodo-4-octene.

(*iii*) 3-Chloro-1-iodohexane. (*iv*) Neopentyl bromide.

(*v*) Isobutyl bromide. (*vi*) *sec*. butyl bromide.

(*vii*) *αω*-Dibromopentane.

66. Name the following :

(*i*) $(CH_3)_3.CBr$. (*ii*) $(CH_3)_2CCl_2$.

(*iii*) $CH_3.CHBr.CH_2Br$. (*iv*) $CH_2Br.CH_2.CH_2Br$.

67. How do you explain the high reactivity of alkyl halides ?
(*Delhi B.Sc. 1977*)

68. The reactivity order of the following compounds is as follows :

Tertiary alkyl bromide > Secondary alkyl bromide > Primary alkyl bromide. Explain. (*Delhi B.Sc. 1977*)

69. How does chloroform react with the following :

(*i*) Acetone, (*ii*) Nitric acid ? (*Delhi B.Sc. 1971*)

70. Give chemical tests to distinguish between ethylene chloride and ethylidene chloride. (*Delhi B.Sc. 1976 ; B.Sc. Hons. Sub. 1977*)

71. Describe the action of aqueous KOH on (*i*) CH_3Cl, (*ii*) CH_2Cl_2, (*iii*) $CHCl_3$, (*iv*) CCl_4. Name the final product in each case.
(*Delhi B.Sc. Hons. Sub. 1976*)

72. Give reactions showing how the following can be obtained from 1-bromopropane :

(*i*) propylene, (*ii*) propanol, (*iii*) nitropropane, (*iv*) butanoic acid.
(*Delhi B.Sc Hons. Sub. 1976*)

73. Give addition and substitution reactions of propene with chlorine. Name the mechanism involved. (*Delhi B.Sc. 1976*)

74. Explain briefly why chlorine atom in vinyl chloride is not reactive.
(*Delhi B.Sc. Hons. 1976*)

75. *t*-Butyl chloride reacts with sodium hydroxide solution by S_N1 mechanism while *n*-butyl chloride reacts by the S_N2 mechanism. Explain why.
(*Kerala B.Sc. 1975*)

76. Give one example where hydrolysis of alkyl halide proceeds according to unimolecular (S_N1) mechanism and one example where it follows bimolecular (S_N2) mechanism. (*Punjab B.Sc. 1976 Supp.*)

77. Give suitable explanations for the following :

(*i*) 2-Butanol on dehydration gives 2-Butene.

(*ii*) Propene on chlorination at 675 to 875 K gives allyl chloride.

(*iii*) Chlorine atom in vinyl chloride is not reactive.

(*iv*) *tert*-Alkyl halides usually react by S_N2 mechanism.
(*Delhi B.Sc. Hons. 1978*)

78. S_N1 type of reactions show racemisation and rearrangement while S_N2 type of reactions show inversion but no rearrangement. Explain.
(*Delhi B.Sc. Hons. 1978*)

79. Explain why chlorine in allyl chloride is reactive while that in vinyl chloride is not reactive (*Andhra B.Sc. 1978*)

80. What is the order of ease of hydrolysis of the halogen in the following compounds ?

(*i*) $(CH_3)_3CCl$; (*ii*) $CH_3CH_2CHICH_3$;
(*iii*) $CH_2=CH.CH_2Br$; (*iv*) $CH_3CH_2CHBrCH_3$;
(*v*) $CH_3CH_2CHI_2$ and (*vi*) $CH_2=CHCl$.
(*Andhra B.Sc. 1978*)

81. How do you explain the following order of reactivity ?

$$CH_3I > CH_3-Br > CH_3Cl$$

82. Why is the reactivity of a tertiary alkyl halide > secondary alkyl halide > primary alkyl halide ?

83. Give mechanism of isomerisation of 1-Bromobutane into 2-Bromobutane and that of *neo*-pentyl chloride into 2-Chloro-methylbutane when heated in the presence of $AlCl_3$ at 573 K.

84. Give equations for the conversion of glycerol into isopropyl iodide.

85. Name various factors which influence mechanism whether S_N1 or S_N2.

86. Summarize distinguishing features of S_N1 and S_N2 mechanisms.

87. What is β-elimination ?

88. Why are S_N1 and E1 competing reactions ?

89. Why does branching at the β-carbon atom tend to favour elimination at the expense of substitution ?

90. Name the factors which tend to favour E2 reactions over the S_N2 reactions

91. With alcoholic potash C_3H_7Br (A) gives C_3H_6 (B) along with some $C_6H_{14}O$ (C) as impurity. B on oxidation gvies $C_2H_4O_2$ (D) + carbon dioxide and water. With hydrobromic acid B gives E, an isomer of A. Identify the compounds A to E.

92. With alcoholic potash $C_4H_8Cl_2$ (A) gives C_4H_6 (B) which reacts with ammoniacal cuprous chloride. Identify compounds A and B.

93. With alkali $C_3H_6Cl_2$ (A) gives C_3H_6O (B) or C_3H_4 (C). C reacts with dilute sulphuric acid containing mercuric sulphate to give C_3H_6O (D) which gives with bromine in alkali, the salt of $C_2H_4O_2$ (E). Identify the compounds A to E.

94 Give structural formulae and IUPAC names of the following organic compounds : (*i*) *sec*. Butyl alcohol ; (*ii*) Diethylcarbinol ; (*iii*) Methylethyl-*iso*-propylcarbinol ; (*iv*) *iso*-Amyl alcohol.

95. Write down the possible structural formulae and IUPAC names of various alcohols represented by the molecular formula $C_5H_{12}O$.

96. Give the reagents used and conditions employed for each step involved to bring about the following conversions :

(*i*) Acetaldehyde from ethanol,

(*ii*) Ethyl acetate from ethanol.

(*iii*) Methanol from ethanol and *vice versa*.

(*iv*) Primary alcohol from secondary alcohol and *vice versa*.
(*Delhi B.Sc. 1976* ; *Rajasthan 1970*)

97. How are the following conversions effected :

(*i*) ethanol into propanol.

(*ii*) 1-propanol into 2-propanol ? (*Delhi B.Sc. Hons. Sub. 1977*)

98. Give chemical tests to distinguish between :

(*i*) *iso*-Propyl alcohol and *n*-propyl alcohol. (*Delhi B.Sc. 1976*)

(*ii*) sec-Butyl alcohol and iso-butyl alcohol. (*Delhi B.Sc. Hons. 1976*)

99. Describe the reaction between ethanol and sulphuric acid under different conditions. (*Delhi B.Sc. 1976*)

100. Give two reactions of 1-propanol in which hydrogen atom of OH group reacts and two reactions in which hydroxyl group as a whole participates. How do you account for such a behaviour ? (*Delhi B.Sc. Hons. 1976*)

101. Outline the stages involved in the following conversions :

(*i*) Isopropyl chloride to *n*-propyl chloride.

(*ii*) Propene to 2, 3-dimethylbutane,

(*iii*) Acetic acid to isopropyl alcohol. (*Delhi B.Sc. Hons. 1976*)

102. Give reasons to explain the fact that tertiary alcohols react rapidly with metallic sodium but more rapidly with organic acids as compared to primary alcohols. (*Delhi B.Sc. Hons. 1976*)

103. Give equations to represent the oxidation of primary, secondary and tertiary alcohols. Name the products in each case. (*Punjabi B.Sc. 1976 Supp.*)

104. Lower members of alcohols are soluble in water. Explain why.
(*Punjabi B.Sc. 1976 Supp*)

105. Alcohols have higher boiling points than corresponding alkanes. Explain why. (*Punjabi B.Sc. 1976 Supp.*)

106. Two bottles are supposed to contain chloroform and allyl alcohol. How will you establish their identity ? Give one test in each case.
(*Delhi B Sc. Hons. 1976*)

107. Two unlabelled bottles contain chloroform and methanol. How would you identify them ? Give one test in each case.
(*Delhi B.Sc. Hons. Sub. 1977*)

108. Why is the boiling point of an alcohol much higher than an alkane of the corresponding molecular weight ? (*Punjab B.Sc. 1974*)

109. Show how would you utilize hydroboration-oxidation procedure to prepare each of the following alcohols.

(a) 1-Hexanol (b) 3,3-Dimethyl 1-butanol.

110. How would you prepare each of the following alcohols by acid-catalysed hydration of the appropriate alkene :

(i) 2-Pentanol (ii) Cyclopentanol

(iii) *tert*-Butyl alcohol.

111. How will you convert :

(i) Propylene into glycerol. (ii) Glycerol into allyl alcohol ?

(Delhi B.Sc. 1977, 76)

112. What happens when glycol is heated with conc H_2SO_4 ?

(Delhi B Sc. Hons 1977)

113. Write structural formulae for

(a) Pentane-1 : 5-diol. (b) 2-Methylpentane-2 : 4-diol

(c) Propylene glycol. (d) Pentamethylene glycol

(e) α : ω-Dihydroxyheptane. (f) Propane-1 : 2 : 3-triol.

(g) 2 : 4-Epoxyhexane.

114. What is an antifreeze ?

115. Why is glycol suitable for use as an antifreeze ?

116. Boiling point of glycol (=400K) is much higher than that of 1-propanol (=370·2K) and 2-propanol (=355·6K) even though all the three compounds have roughly the same molecular weight. How can you account for this fact ?

117. Specific gravity increases from methanol (=0·792) to glycol (=1·113 and further to glycerol (=1·261). How can you account for the progressive increase in specific gravity ?

118. What are the difficulties encountered in the preparation of di-*tert* Butyl ether by the Williamson's method ? *(Delhi B Sc Hons 1976)*

119. How will you convert *tert* butyl alcohol into di-*tert* butyl ether ?

(Delhi B Sc. Hons. 1976 , Madras B.Sc. 1978)

120. What test would you perform to distinguish between : *n*-butyl alcohol and diethyl ether ? *(Delhi B Sc. Hons. 1976 ; Sub. 1978)*

121 How is ethanol converted into diethyl ether by Williamson's process ? Write the structures of other ethers isomeric with it.

(Delhi B Sc. Hons. Sub. 1976)

122. Name various ethers represented by the molecular formula $C_4H_{10}O$ and write their structural formulae.

123. State how you can distinguish by chemical means between Diethyl ether and methyl propyl ether. *(Agra B Sc. 1970)*

124. Account for the following :

(a) Presence of acid is necessary for the cleavage of ethers.

(b) Sometimes explosion occurs during distillation of an ether sample.

125. How is peroxide in ether detected and removed.

126. C_2H_5Br is freed from traces of ether by shaking with conc. H_2SO_4 Explain why ?

127. How will you distinguish between an alcohol and an ether ?

(Delhi B.Sc. 1978 Supp.)

128. Give reasons for the following :

(*i*) Alcohols have higher boiling points than the corresponding isomeric ethers.

(*ii*) Diethyl ether behaves as a base. (*Delhi B Sc Hons. Sub. 1978*)

129. Write structural formulae of the isomeric ethers of the molecular formula $C_4H_{10}O$ and name them according to the IUPAC system. (*Madras B.Sc. 1978*)

130. Write giving mechanism what you know about the following cleavage of ether molecules by acids. (*Punjab B Sc. 1974, 75, 76*)

131. How do you account for high dipole moment of aldehyde and ketones ?

132. Write IUPAC names of the compounds whose formulae are given below :

(*i*) C_6H_5CHO (*ii*) $CH_3CH_2COCH_2CH_3$

(*iii*) $CH_3.C_6H_4.CHO$ (*iv*) $CH_3COCH_2CH_3$

133 Write the formulae of various carbonyl compounds having the molecular formula C_4H_8O and give their trivial as well as IUPAC names.

134 How is an aldehyde obtained from an acid chloride ?

135 How is ketone obtained from an acid chloride ?

136 In what respect is dialkylcadmium superior to Grignard reagent for the preparation of a ketone from an acid chloride ?

137 Solubility of carbonyl compounds decreases with the increase in their molecular masses Explain why ?

138 Boiling points of aldehydes lie between parent alkanes and corresponding alcohols. How do you account for it ?

139 What do you understand by nucleophilic addition to the carbonyl group ? Write mechanism

140. How do you represent and account for acid-catalysed nucleophilic addition to the carbonyl group ?

141. Write mechanism for the nucleophilic addition of HCN and $NaHSO_3$ to >C=O group

142. What is aldol condensation ?

143 What is Tollen's reagent ? How does it react with acetaldehyde ?

144 Write a short note on :

(*i*) Clemmensen reduction.

(*ii*) Wolff-Kishner reduction

(*iii*) Meerwein Ponndorf reduction

145. How do you account for the following .

(*a*) In the laboratory preparation of acetaldehyde by oxidation of ethanol acetaldehyde is distilled out continuously.

(*b*) Dialkylcadmium is considered superior to Grignard reagent for the preparation of a ketone from an acid chloride.

(*c*) $NaHSO_3$ is used for the purification of aldehydes and ketones.

146. Write two reactions showing difference between HCHO and CH_3CHO

147. Give two chemical properties in which CH_3CHO and CH_3COCH_3 differ.

148 Give chemical tests to distinguish between acetaldehyde and acetone. (*Delhi B Sc. 1976*)

149. What happens when acetaldehyde is treated with dilute sodium hydroxide solution ? (*Delhi B.Sc. 1976*)

150. Explain briefly why chloral forms stable hydrate.
(Delhi B.Sc. Hons. 1976)

151. Write equation to show Cannizzaro's reaction. *(Delhi B.Sc. 1976)*

152. Explain intermolecular hydride transfer in Cannizzaro reaction.
(Delhi B.Sc. Hons. 1976)

153. CH_3COCH_3 reacts with phenylhydrazine but CH_3CONH_2 does not, though both have the carbonyl group. Explain why. *(Kerala B.Sc. 1975)*

154. Discuss the mechanism of pinacol-pinacolone rearrangement
(Delhi B.Sc. Hons. 1976 ; Nagpur B.Sc. 1974 Supp.)

155. Why does acetaldehyde not undergo Cannizzaro reaction ?
(Delhi B.Sc. Hons. 1977)

156. Write a short note on Rosenmund's reaction. *(Madras B.Sc. 1976)*

157. How may acetone be obtained from acetic acid ?
(Madras B.Sc. 1978)

158. How does

(*i*) hydroxylamine react with acetaldehyde ?

(*ii*) formaldehyde react with ammonia ? *(Madras B.Sc. 1978)*

159. Indicate the method of converting acetone into

(*i*) chloroform, (*ii*) mesitylene,

(*iii*) isopropyl alcohol, (*iv*) α-hydroxy-isobutyric acid.
(Madras B.Sc. 1978)

160. How may acetaldehyde be converted into lactic acid ?
(Madras B.Sc. 1978)

161. What is a carboxyl group ? Why is it so called ?

162. Lower carboxylic acids are very soluble in water. Solubility decreases with increase in molecular mass. Explain, why ?

163. Melting point of an acid with even number of carbon atoms is higher than those of its immediate neighbours with odd number of carbon atoms. How can you account for this fact ?

164. Boiling point of an acid is higher than an alcohol with same number of carbon atoms. Give reason, why ?

165. Which is more acidic of each pair :

(*a*) $CH_2ClCOOH$ and $CH_2BrCOOH$

(*b*) $CHCl_2COOH$ and CH_3COOH

(*c*) CH_3COOH and $HCOOH$

166. Complete the following equations :

(*i*) $C_2H_5MgBr \xrightarrow[(ii)\ H^+]{(i)\ CO_2}$

(*ii*) $C_6H_5COONa + NaOH \longrightarrow$

(*iii*) $CH_3CH_2COOH \xrightarrow{LiAlH_4}$

167. Arrange the acids given in each set in the order of increasing acidity :

(*a*) CH_3CH_2COOH, $CH_3CHClCOOH$, $CH_3CHFCOOH$

(*b*) CH_3COOH, $CH_2ClCOOH$, $CHCl_2COOH$, CCl_3COOH

(*c*) $CH_3CHClCOOH$, CH_2ClCH_2COOH

168. In acrylic acid $CH_2{=}CH{-}COOH$, the addition of HCl takes place contrary to Markownikoff's rule but in the acid structure

$$CH_2=CH—CH_2—CH_2COOH$$

the addition is in accordance with the rule. Explain. (*Delhi B.Sc. Hons. 1977*)

169. The labels of four bottles supposed to contain respectively acetone, formic acid, methyl alcohol and chloroform have been removed. By what chemical tests would you be able to put labels on these bottles ? (*Jabalpur B.Sc. 1976*)

170. Though fatty acids have >C=O group in them, yet they do not form oximes. Explain. (*Delhi B.Sc. Hons. 1976*)

171. An alcohol does not dissociate to give hydrogen ions, while a carboxylic acid does, when both contain the hydroxyl group. Explain. (*Delhi B.Sc. Hons. Sub. 1977*)

172. β-Keto-acids undergo decarboxylation easily. Explain why. (*Kerala B.Sc. 1975*)

173. Monochloroacetic acid is a stronger acid than monobromoacetic acid. Give reasons. (*Madurai B.Sc. 1976 Supp.*)

174. Starting from propionic acid how are the following prepared ?

(*i*) Propionamide. (*ii*) Propionic anhydride.

(*iii*) Diethyl ketone. (*Madurai B.Sc. 1976 Supp.*)

175. Formic acid is stronger acid than acetic acid. Explain why. (*Madurai B.Sc. 1976*)

176. Trichloroacetic acid is a stronger acid than acetic acid. Account for this. (*Madras B.Sc. 1976 Supp.*)

177. How is oxalic acid converted into formic acid ? (*Madras B.Sc. 1978*)

178. Give an example to illustrate the reducing property of formic acid. (*Madras B.Sc. 1978*)

179. How would you effect the following conversions :

(*i*) 1-Bromopropane into butanoic acid ?

(*ii*) Malonic acid into acetic acid ? (*Madras B.Sc. 1978*)

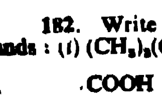
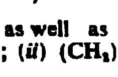
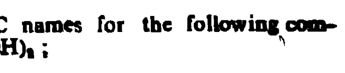
180. How does acrylic acid react with

(*i*) bromine, (*ii*) dilute aqueous potassium permanganate ? (*Madras B.Sc. 1978*)

181. Starting from acetic acid how will you obtain

(*i*) monochloracetic acid, (*ii*) acetamide ? (*Madras B.Sc. 1978*)

182. Write common as well as IUPAC names for the following compounds : (*i*) $(CH_2)_3(COOH)_2$; (*ii*) $(CH_2)_4(COOH)_2$;

(*iii*)

$$CH_2\begin{array}{l}COOH\\ COOH\end{array}$$
; (*iv*)

$$\begin{array}{l}CHCOOH\\ \|\\ CHCOOH\end{array}$$
; (*v*)

$$HOOC.\underset{\displaystyle CH_3}{CH}.CH_2.CH_2.\underset{\displaystyle Cl}{CH}.COOH$$

183. What is the action of alkaline $KMnO_4$ on—

(*i*) maleic acid. (*ii*) fumaric acid ? (*Delhi B.Sc. 1976*)

184. Based on the orbital concept of covalent bond explain the existence of geometric isomers. (*Delhi B.Sc. 1976*)

185. What is the action of heat on the following

(*i*) Malonic acid, (*ii*) Glutaric acid,

(*iii*) Oxalic acid, (*iv*) Ammonium oxalate,

(*v*) Ammonium succinate, (*vi*) Malic acid ?

186. How is oxalic acid converted into formic acid ? (*Madras B.Sc. 1977*)

187. Starting from malic acid how would you prepare maleic and fumaric acids ? *(Delhi B Sc. Hons. Sub. 1977 Supp.)*

188. How would you distinguish between maleic and fumaric acids ? *(Madras B.Sc. 1974 ; Delhi B.Sc. Hons. Sub. 1978 Supp.)*

189. What products are obtained when malic acid is

(*i*) oxidised and (*ii*) reduced. *(Madras B.Sc. 1978)*

190. First hydrogen atom in oxalic acid ionizes 1000 times more readily than the second hydrogen atom. Explain, why ?

191. What is the action of (*i*) heat, (*ii*) sodium hypochlorite, (*iii*) nitrous acid, and (*iv*) malonic ester on urea ? *(Delhi B.Sc. 1976)*

192. Give the mechanism of Hofmann hypobromite reaction. *(Delhi B.Sc. Hons. Sub. 1976)*

193. Explain briefly why acetyl chloride is a stronger acetylating agent than acetic acid. *(Delhi B.Sc. Hons. 1977)*

194. Why acetyl chloride is a better acetylating agent than acetic anhydride ? Explain, giving reasons. *(Delhi B.Sc. Hons. 1976)*

195. Give reasons why acetamide is very slowly hydrolysed with water but rapidly in the presence of an acid or alkali. *(Punjab B.Sc. 1975 Supp.)*

196. Explain why amides ($RCONH_2$) are much weaker bases (rather somewhat acidic than amines). *(Guru Nanak Dev B.Sc. 1976 Supp.)*

197. Explain why S_N2 reaction takes place much readily at an acyl carbon than an alkyl carbon. *(Guru Nanak Dev B.Sc. 1976)*

198. Give the probable mechanism of the alkaline hydrolysis of an ester. *(Punjab B.Sc. 1976 Supp.)*

199. Complete the equation given below, mentioning the name of the reaction concerned

$$CH_3CONH_2 \xrightarrow{OH^-}$$ *(Punjab B Sc 1976 Supp.)*

200 What is Hofmann's degradation ? *(Madurai B Sc. 1978, 77)*

201. How will you distinguish between acetamide and urea ? *(Kanpur B.Sc. 1978)*

202. How will you show that acetamide possesses an amide group ? *(Kanpur B Sc. 1977)*

203. Write a note on Biuret reaction. *(Madras B.Sc. 1978)*

204. Explain why urethane is prepared by the reaction of isocyanate and absolute ethyl alcohol. *(Delhi B Sc. 1978)*

205. How can nitroalkanes be distinguished from alkyl nitrites ? *(Delhi B Sc. 1976 Supp.)*

206. Why are primary nitroalkanes acidic in nature ? *(Delhi B Sc. 1976)*

207. What are oils, fats and soap ? *(Guru Nanak Dev B.Sc. 1971)*

208 How does soap solution remove dirt particles from cloth ? *(Guru Nanak Dev B.Sc. 1971*

209. Sketch the structural formulae of (*i*) Ethyl acetate and (*ii*) Methyl propionate. *(Guru Nanak Dev B.Sc. 1971)*

210. How do you explain the formation of ethyl nitrite and nitroethane when ethyl bromine reacts with potassium nitrite and silver nitrite respectively ?

211. What are drying oils ?

212. Give electronic mechanism of Esterification. *(Kerala B.Sc. 1957 ; Delhi 1976)*

213. Define the saponification value of a fat and explain its significance. *(Madurai B.Sc. 1976 October)*

214. How was it established that esterification involves the cleavage of the O—H bond of the alcohol and C—OH bond of the acid ? *(Delhi B.Sc. Hons. 1977)*

215. Nitromethane dissolves in alkali. Explain why. *(Andhra B.Sc. 1978)*

216. Nitromethane slowly dissolves in aqueous alkali but methane does not do so. Explain. *(Madras B.Sc. 1978)*

217. Compare the behaviour of primary, secondary and tertiary nitroalkanes towards nitrous acid. *(Madras B.Sc. 1978)*

218. Discuss the mechanism of hydrolysis of esters. *(Andhra B.Sc. 1978,*

219. Give two characteristic reactions of ethyl nitrite and nitroethane. *(Madras B.Sc. 1978)*

220. Give the mechanism for an ester formation. *(Srivenkateswara B.Sc. 1978)*

221. How do primary, secondary and tertiary amines differ in their reaction towards nitrous acid ? *(Punjabi B.Sc. 1976)*

222. Give two chemical properties of Ethylamine. *(Punjabi B.Sc. 1976)*

223. Using Hinsberg's reagent, give a scheme to separate a mixture of *n*-propylamine, diethylamine and triethylamine into its constituents. *(Delhi B.Sc. 1976)*

224. How will you separate the constituents of a mixture of methylamine and dimethylamine ? Give one reaction to distinguish them. *(Delhi B.Sc. Hons. 1976)*

225. How are primary, secondary and tertiary amines distinguished from one another ? (Only two tests are required.) *(Delhi B.Sc. 1976 Supp.)*

226 The amino group in ethylamine is basic whereas that in acetamide is not. Explain, why ? *(Delhi B.Sc. Hons. 1976)*

227. Write a note on comparative strength of the primary, secondary and tertiary amines. *(Delhi B.Sc. 1977)*

228. Explain how you would proceed to distinguish between : Methyl cyanide and Methyl isocyanide. *(Agra B.Sc. 1970)*

229. Give electronic mechanism for the reaction of ethyl iodide with (*i*) KCN and (*ii*) AgCN.

230. What is an active methylene group ? Give structures of three compounds having such a group. *(Delhi B.Sc. Hons. 1977 ; B.Sc. 1976 Supp.)*

231. Why is the keto form of acetoacetic ester more stable than its enolic form ? *(Delhi B.Sc. Hons. 1977)*

232. How can the following compounds be prepared from *either* acetoacetic ester *or* malonic ester ?

(*i*) Benzylacetone, (*ii*) $CH_3COCH_2CH_2COOH$,
(*iii*) Barbituric acid, (*iv*) Glutaric acid.
(Delhi B.Sc. Hons. 1977)

233. What is the action of alkali on :

(*i*) Mono-, di- and trichloroacetic acids.

(*ii*) α-, β- and γ-chlorobutyric acids.

234. What happens when—

(*i*) Trichloroacetic acid is heated with soda lime.

(*ii*) Formaldehyde is reacted with ammonia. ***(Jabalpur B.Sc. 1976)***

235. What do you understand from isoelectric point ? *(Jabalpur B.Sc. 1976*

236 Trichloroacetic acid is a very strong acid. Explain why. *(Calicut B.Sc. 1975)*

237. How would you prove the amphoteric behaviour of aminoacids ? *(Agra B.Sc. 1973)*

238. What is the action of heat on glycine ? *(Agra B.Sc. 1973)*

239. Monochloroacetic acid is a stronger acid than monobromoacetic acid. Explain why. *(Madras B.Sc. 1976 October)*

240. Trichloroacetic acid is a stronger acid than acetic acid. *(Madras B.Sc. 1976 Sept.)*

241. Explain why proteins in solution at low *p*H will migrate towards the cathode while in solutions of high *p*H these proteins migrate towards the anode. *(Bangalore B.Sc. 1974)*

242. Chloroacetic acid is a better proton donor compared to acetic acid. Give satisfactory explanation for this fact. *(Osmania B.Sc. 1975)*

243. How can a β-amino acid be obtained from : (*i*) an aldehyde, and (*ii*) a halogen-substituted acid ? *(Delhi B.Sc. 1976 Supp.)*

244. How would you show that acetic acid is a β-hydroxy acid ? *(Delhi B.Sc. 1976 Supp.)*

245. How would you synthesise tartaric acid, starting from acetylene ? Indicate the reagent and conditions employed for each step involved. *(Delhi B. Sc. 1976)*

246. What happens when tartaric acid is treated with (*a*) hydriodic acid, (*b*) conc. H_2SO_4, (*c*) hydrobromic acid, (*d*) PCl_5 ? *(Delhi B.Sc. 1976, 77)*

247. Explain any *four* of the following :

(*i*) Fumaric acid has a higher melting point than maleic acid.

(*ii*) Malonic acid undergoes easy decarboxylation.

(*iii*) Maleic acid gives anhydride on heating while fumaric does not.

(*iv*) Benzoic acid is more acidic than acetic acid.

(*v*) Phenols are stronger acids than alcohols.

(Delhi B.Sc. Hons. 1980)

248. Explain any two of the following :

(*i*) Allyl chloride is hydrolysed more readily than propyl chloride.

(*ii*) Acetamide has slight acetylating action, whereas acetyl chloride is a vigorous acetylating agent.

(*iii*) Sodium reacts with acetylene not with ethylene.

(*iv*) Amines are higher boiling compounds than hydrocarbons of corresponding molecular weight, but have lower boiling points than corresponding alcohols.

(Delhi B.Sc. 1980)

249. Explain the following :

(*a*) Carboxylic acid and esters of carboxylic acids do not respond to the dinitrophenylhydrazine test although both contain the carbonyl group.

(*b*) Alkyl chlorides and allyl chloride give a precipitate of AgCl on heating with alcoholic $AgNO_3$ whereas vinyl chloride does not.

(*c*) NH_3 is more basic than trimethylamine but less basic than methylamine.

(*d*) Propylene on treatment with HBr in presence of peroxide gives *n*-propyl bromide. *(Delhi B.Sc. Hons. 1981)*

250. Explain any *two* of the following :

(*i*) The boiling point of ethyl alcohol is higher than that of dimethyl ether, although both have the same molecular weight.

(*ii*) Propionic acid is a weaker acid than formic acid.

(*iii*) Actone is less reactive than actaldehyde.

(*iv*) Methylamine is stronger base than ammonia. (*Delhi B.Sc. 1981*)

OBJECTIVE TYPE

(A) SELECTION TEST TYPE :

Choose the correct alternative(s) out of the suggested ones as answer in the following questions ;

1. A nucleophile being an electron-rich species must possess :

(*a*) An overall negative charge. (*b*) An overall positive charge. (*c*) An unpaired electron. (*d*) An unshared pair of electrons.

2. In the rearrangement of a carbonium ion to form a more stable carbonium ion, the migrating group leaves :

(*a*) With its electron pair, (*b*) Without its electron pair, (*c*) As a free radical, (*d*) As a di-radical.

3. Which of the following statements concerning carbonium ions is not correct ?

(*a*) Primary carbonium ions are more stable than secondary.

(*b*) Secondary free radicals are more stable than primary.

(*c*) Tertiary free radicals are more stable than secondary.

(*d*) Tertiary carbonium ions are more stable than primary.

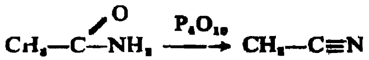
4. The number of possible isomers of monochloro derivatives of 2-methylbutane is :

(*a*) one, (*b*) two, (*c*) three, (*d*) four.

5. Which of the following reagents may be labelled as electrophilic?

(*a*) NH_3, (*b*) CH_3OH, (*c*) BCl_3, (*d*) $AlCl_4$.

6. The change in hybridisation of carbon in the dehydration of acetamide given below is :



$$CH_3—\overset{O}{\overset{\|}{C}}—NH_2 \xrightarrow{P_4O_{10}} CH_3—C\equiv N$$

(*a*) sp^3 to sp^2. (*b*) sp^3 to sp. (*c*) sp to sp^2. (*d*) sp^2 to sp.

7. Which of the statements given below is not characteristic of a reaction taking place by free radical mechanism :

(*a*) It may be initiated by heat.

(*b*) The final product is derived from the most stable free radical.

(*c*) One mole of product is obtained from each mole of free radical initiated.

(*d*) Nature of solvent (polar or non-polar) has practically no effect on it.

8. Hydrolysis of *tert.* butyl bromide, $(CH_3)_3CBr$ is a first order reaction. One reason for this is that :

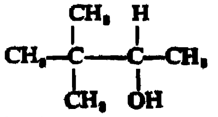
(*a*) the intermediate carbo-cation is stabilised by solvation ;

(*b*) the intermediate *tert*-butyl carbo-cation is relatively easily formed ;

(*c*) the product *tert*-butyl alcohol is thermodynamically stable ;

(*d*) Walden inversion takes place.

9. Which of the following is the major product of dehydration of the following alcohol :



$$CH_3—\underset{CH_3}{\overset{CH_3}{C}}—\underset{OH}{\overset{H}{C}}—CH_3$$

(*a*) 3,3-Dimethyl-1-butene ; (*b*) 2,3-Dimethyl-1-butene ; (*c*) 2, 3-Dimethyl-2-butene ; (*d*) 3-Methyl-2-pentene.

10. Chlorination of propylene at 750K produces mainly :

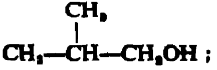
(*a*) $CH_2ClCHClCH_2Cl$; (*b*) $CH_3CCl=CHCl$;

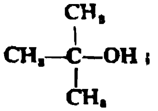
(*c*) $CH_2ClCH=CH_2$; (*d*) $CH_3CHClCH_2Cl$.

11. Which of the following bases is most likely to favour S_N1 reaction rather than S_N2 reaction in the hydrolysis of an alkyl halide ?

(*a*) OH^- ; (*b*) OEt^- ; (*c*) H_2O ; (*d*) NH_2^-.

12. In the acid catalysed dehydration to the corresponding alkene, which of the following butyl alcohols is most easily dehydrated

(*a*) 
$CH_3-\overset{CH_3}{\overset{|}{C}H}-CH_2OH$;

(*b*) 
$CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-OH$;

(*c*) $CH_3.CH_2.CH_2.CH_2OH$; (*d*) $CH_3CH_2.CHOH.CH_3$.

13. Normally S_N2 reactions proceed with :

(*a*) retention of configuration ; (*b*) Walden inversion ;

(*c*) racemisation ; (*d*) racemisation and Walden inversion.

14. Final product of the reaction between 1-butyne and HI is :

(*a*) 2, 2-Diiodobutane. (*b*) 1, 2-Diiodobutane. (*c*) 1, 1-Diiodobutane. (*d*) 1, 1, 2, 2-tetraiodobutane.

15. A hydrocarbon with molecular formula, C_4H_6 reacts with bromine readily and gives a white precipitate with ammoniacal silver nitrate solution. Treatment with dil H_2SO_4 solution containing $HgCl_2$ gives 2-butanone. The hydrocarbon is :

(*a*) 2-Butyne. (*b*) 1-Butene. (*c*) Cyclobutene. (*d*) 2-Butyne.

16. On bubbling 1-butyne through dil. H_2SO_4 containing mercuric chloride the main product is :

(*a*) Butanone. (*b*) 1-Butanol. (*c*) 2-Butanol. (*d*) 1, 2-Butanediol.

17. An unsaturated hydrocarbon X (C_4H_6) on partial reduction with hydrogen in presence of palladium gives Y (C_4H_8). X gives a precipitate with ammoniacal cuprous chloride solution.

(*a*) X is 1, 3-butadiene and Y is 1-butene.

(*b*) X is 1, 3-butadiene and Y is 2-butene.

(*c*) X is 1-butyne and Y is 1-butene.

(*d*) X is 2-butyne and Y is 2-butene.

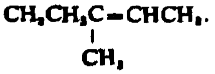
18. Which one of the following products is not probable in the reaction between ethylene and bromine water containing NO_3^- and Cl^- ?

(*a*) CH_2BrCH_2Cl ; (*b*) CH_2ClCH_2Cl ;

(*c*) CH_2BrCH_2Br ; (*d*) $CH_2BrCH_2ONO_2$.

19. The alkene which produces acetaldehyde and 2-butanone on ozonolysis is :

(*a*) $(CH_3)_2CHCH=CHCH_3$. (*b*) $CH_3CH_2CH_2CH=CH_2$.

(*c*) 
$CH_3CH_2\underset{CH_3}{\underset{|}{C}}=CHCH_3$. (*d*) $C_6H_5CH=C(CH_3)CH_2CH_3$.

20. Which one of the following organic compounds would give iodoform reaction ?

(*a*) $CH_3CH_2CH_2CHO$ (*b*) $CH_3CH_2COCH_3$

21. Which one of the following compounds gives an addition product with HI not according to Markownikoff rule :

(*a*) $CH_3CH=CH_2$. (*b*) $CF_3CH=CH_2$

(*c*) $CH_3(CH_2)_2CH=CH_2$. (*d*) $CF_3(CH_2)_2CH=CH_2$.

22. The following reaction is a/an :

$CH_3CHO+NH_2-NH_2 \longrightarrow CH_3-CH=N-NH_2+H_2O$

(*a*) elimination reaction (*b*) condensation reaction

(*c*) nucleophilic substitution (*d*) electrophilic substitution.

23. Which one of the following is most readily attacked by nucleophiles ?

(*a*) C_6H_5CHO, (*b*) CH_3CHO, (*c*) HCHO, (*d*) CH_3COCH_3.

24. The order of reactivity of the following alkenes towards electrophilic attack is :

(*i*) $CH_3CH=CH_2$, (*ii*) $CH_2=CHCl$.

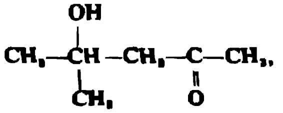
(*iii*) $CH_2=CH_2$ (*iv*) $(CH_3)_2C=CH_2$

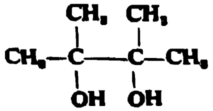
(*a*) (*i*) > (*iii*) > (*ii*) > (*iv*) ; (*b*) (*i*) > (*iii*) > (*ii*) > (*iv*) ;

(*c*) (*i*) > (*iv*) > (*iii*) > (*ii*) ; (*d*) (*iv*) > (*i*) > (*iii*) > (*ii*)

25. Major product obtained when acetone is refluxed with Mg followed by hydrolysis with dilute acid, is :

(*a*) $CH_3-CH_2-CH_3$, (*b*) $CH_3-CHOH-CH_3$.

(*c*) 
$CH_3-\underset{CH_3}{\overset{OH}{CH}}-CH_2-\underset{O}{\overset{}{\underset{\|}{C}}}-CH_3$,

(*d*) 
$CH_3-\underset{OH}{\overset{CH_3}{C}}-\underset{OH}{\overset{CH_3}{C}}-CH_3$

26. Among the following acids the strongest acid is :

(*a*) CH_3COOH. (*b*) CH_2ClCH_2COOH,

(*c*) $CH_2ClCOOH$, (*d*) CH_3CH_2COOH.

27. On arranging CH_3COCl, CH_3CONH_2 and $CH_3COOC_2H_5$ in the decreasing order of reactivity towards nucleophiles, we get

(*a*) $CH_3COCl > CH_3CONH_2 > CH_3COOEt$

(*b*) $CH_3COCl > CH_3COOEt > CH_3CONH_2$

(*c*) $CH_3COOEt > CH_3CONH_2 > CH_3COCl$

(*d*) $CH_3CONH_2 > CH_3COCl > CH_3COOEt$.

28. The strongest base among the following compounds is :

(*a*) $(C_2H_5)_2NH$ (*b*) $C_2H_5NH_2$

(*c*) $C_6H_5NH_2$ (*d*) CH_3CONH_2.

29. Of the following compounds the one/ones which give(s) nitrogen when treated with $NaNO_2$ and dilute HCl, is/are :

(*i*) $CH_3NHC_2H_5$ (*ii*) $(CH_3)_3N$

(*iii*) $(CH_3)_2CHNH_2$ (*iv*) $C_6H_5CH_2NH_2$

(*a*) (*i*) and (*ii*), (*b*) (*iv*), (*c*) (*iii*) and (*iv*), (*d*) none.

30. Out of the compounds given below, the one which is hydrolysed by water with greatest ease is :

(*a*) CH_3CONH_2 (*b*) $CH_3COOC_2H_5$

(*c*) CH_3COCl (*d*) $(CH_3CO)_2O$.

31. Out of the various reagents given below, acetamide reacts with maximum ease with :

(a) C_2H_5OH (b) $C_6H_5NH_2$

(c) H_2O (d) aqueous solution of NaOH.

32. Acetic anhydride is prepared in the laboratory by heating sodium acetate with :

(a) Zinc dust. (b) Conc.H_2SO_4

(c) Acetyl chloride. (d) Ethyl chloride.

33. Compound X having molecular formula C_3H_9N when subjected to exhaustive methylation followed by treatment with moist silver oxide and heating gives ethylene as the major product. X is :

(a) $CH_3—N(CH_3)_2$ (b) $CH_3—CH(NH_2)—CH_3$

(c) $CH_3CH_2CH_2NH_2$ (d) $CH_3CH_2NHCH_3$

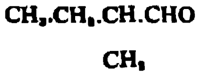
34. An ester X when heated with aqueous alkali gave an alcohol Y and the salt of the acid Z. Y gave a positive iodoform test. Z decolorised an acidified solution of $KMnO_4$. The ester X is :

(a) $CH_3COOC_2H_5$ (b) CH_3COOCH_3

(c) $HCOOCH_3$ (d) $HCOOC_2H_5$.

35. Which of the following compounds will undergo Cannizzaro's reaction when treated with an alkali ?

(a) $CH_3.CH_2.CH_2.CH_2CHO$, (b) $(CH_3)_2CH.CH_2CHO$,

(c) 

$$CH_3.CH_2.\underset{CH_3}{CH}.CHO$$

(d) $(CH_3)_3C-CHO$

36. Starting material to synthesise 2-methyl-2-butanoic acid is

(a) $(CH_3)_3C-OH$ (b) $CH_3CH_2CH_2CHO$

(c) $CH_3CH_2COCH_3$ (d) $(CH_3)_2$ CH—CHO

37. Methyl ketones are usually characterised through :

(a) The Tollen's reagent, (b) The Schiff's test,

(c) The Benedict's solution, (d) The bromine test,

(e) The iodoform test.

.KEY

1. (d)	2. (a)	3. (a)	4. (d)	5. (c)
6. (d)	7. (c)	8. (b)	9. (c)	10. (c)
11. (c)	12. (b)	13. (b)	14. (a)	15. (d)
16. (a)	17. (c)	18. (b)	19. (c)	20. (b)
21. (b)	22. (b)	23. (c)	24. (d)	25. (d)
26. (c)	27. (b)	28. (a)	29. (c)	30. (c)
31. (d)	32. (c)	33. (d)	34. (d)	35. (d)
36. (c)	37. (d)			

B) TRUE-FALSE TYPE :

Write the word True, False or Don't know against each statement given below :

1. Methane undergoes addition reactions.

2. Electrolysis of an aqueous solution of sodium acetate gives ethane. This is an example of Wurtz synthesis.

3. Formation of divinylacetylene from acetylene is an example of cyclic polymerisation.

5. Alkyl halides on reduction with zinc-copper couple and alcohol give alkenes.

6. Chloral is an aldehyde.

7. The ease of dehydration of alcohols is in the order :

Primary > Secondary > Tertiary

8. The weaker the carbon-halogen bond, the greater the reactivity of the alkyl halide. Hence the reactivity sequence is :

$$R{-}I > R{-}Br > R > Cl > R > F$$

9. An alcohol can accept a proton to give protonated alcohol, *i.e.*, it can act as a base.

10. The acidity of alcohols has the following sequence :

Methanol > primary > secondary > tertiary

11. The more stable alkene is the preferred product of dehydration of alcohols.

12. Vinyl alcohol and acetaldehyde are isomers.

13. The ease of formation of carbonium ion during dehydration of alcohol follows the sequence :

Primary > secondary > tertiary

14. Acetone gives a pink colour with Schiff's reagent.

15. Esters can be obtained by Grignard reaction.

16. Hydrolysis of a Grignard reagent gives an alkene.

17. Bonding in methane molecule involves sp^3 hybridisation.

18. During unimolecular nucleophilic substitution reaction (S_N1) in alkyl halides, the departing group leaves the molecule, before the entering group is attached to the molecule. A positive charge develops on the carbon atom.

19. During S_N2 reaction, the departing group leaves the molecule only *after* the entering group is attached to the molecule.

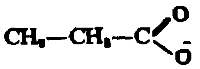
20. The nucleophilic reagents are electron-rich species (and basic in character).

21. A carbanion is formed when carbon atom acquires a positive charge.

22. Electrophilic substitution or addition is a stepwise process involving an intermediate carbonium ion.

23. Hydrogen bonding in alcohols is the cause for their high boiling points.

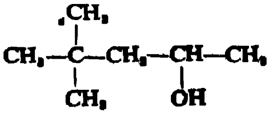
24. Electron delocalisation is possible in



25. An acid chloride is a stronger electrophile than an acid.

26. Chloroacetic acid is stronger than acetic acid.

27. The IUPAC name for



$$CH_3{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}{-}CH_2{-}\underset{\underset{OH}{|}}{CH}{-}CH_3$$

is 2, 2-dimethylpentan-4-ol.

28. Addition of water to an alkene is an electrophilic addition.

29. Bromination is an example of general relationship between reactivity and selectivity. It is due to relatively low reactivity of bromine atoms.

30. Chlorination of an alkene is suitable for the preparation of an alkyl halide.

31. Halogenation of alkanes is a free-radical chain substitution reaction.

32. In the reaction

$$CH_3Cl + OH^- \longrightarrow CH_3OH + Cl^-$$

(*a*) the rate of reaction is independent of the concentration of OH^-.

(*b*) the OH^- attacks the carbon from the side away from the Cl atom.

33. Bromination of propionic acid in presence of phosphorus gives

$$CH_3CHBrCOOH$$

34. Addition of HBr to $CH_2{=}CH.COOH$ gives $CH_2Br{-}CH_2.COOH$.

35. Chlorination of propene at high temperature gives $ClCH_2{-}CH{=}CH$

36. Ethyl chloride when treated with alc. KOH gives ethyl alcohol.

37. In the dehydrohalogenation of an alkyl halide, more stable the alkene, the more easily it is formed.

38. α-aminoacids on heating lose a molecule of water to produce a cyclic anhydride.

39. β-hydroxypropionic acid on heating gives a lactide.

40. Urethan is $NH_2COOC_2H_5$.

KEY

1.	F	2.	F	3.	F	4.	T	5.	F
6.	T	7.	F	8.	T	9.	T	10.	T
11.	T	12.	T	13.	F	14.	F	15.	T
16.	T	17.	F	18.	T	19.	T	20.	T
21.	F	22.	T	23.	T	24.	T	25.	T
26.	T	27.	F	28.	T	29.	T	30.	F
31.	T	32.	F	33.	T	34.	T	35.	T
36.	T	37.	T	38.	T	39.	F	40.	T

(C) COMPLETION TEST TYPE :

Complete the following equations :

1. $CH_3CHBrCH_2CH_3 + KOH \xrightarrow[\text{Heat}]{C_2H_5OH}$

2. $Br{-}CH_2{-}CH_2{-}Br \xrightarrow{?} C_2H_4$

3. $CH_3I + (CH_3)_2CHONa \longrightarrow$

4. $CH_3CH{=}CH.CH_2Br \xrightarrow{OH^-}$

5. $CH_3.CH_2.CH_2.CHBr.CH_3 + (CH_3)_3CO^-K^+ \longrightarrow$

6. $CH_3.CH_2.CH_2Br \xrightarrow{KOH(alc)} A \xrightarrow{H_2O,\ H^+} B \xrightarrow{Cu,\ 570K} C$

7. $HCHO \xrightarrow{KOH}$

8. $HOOC.(CH_2)_3COOH \xrightarrow{Ac_2O}$

9. Chloracetic acid $\xrightarrow{NaOH} A \xrightarrow{CN^-} B \xrightarrow[(ii)\ H^+]{(i)\ H_2O} C \xrightarrow[H^+]{C_2H_5OH} D$

10. $C_2H_5OH \xrightarrow{[O]} (A) \xrightarrow{[O]} (B) \xrightarrow[H^+]{C_2H_5OH} (C)$

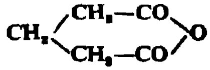
11. $CH_3COOC_2H_5 \xrightarrow{NH_3} (A) \xrightarrow{P_4O_{10}} (B) \xrightarrow[H^+]{H_2O} (C)$

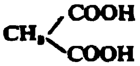
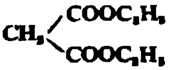
12. $CH_3COOH \xrightarrow{CaCO_3} (A) \xrightarrow{heat} (B) \xrightarrow{NaHSO_3} (C)$

13. $CH_3CHO \xrightarrow{[O]} (A) \xrightarrow{PCl_5} (B) \xrightarrow{CH_3COONa} C$

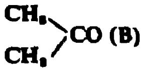
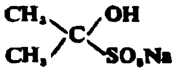
14.* $CH_3CHO \xrightarrow{HCN} A \xrightarrow{NH_3} B \xrightarrow{H_2O} C$

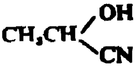
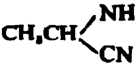
KEY

1. $CH_3.CH=CH.CH_3$ 2. KOH (alc) or $NaNH_2$
3. $(CH_3)_2CHOCH_3$ 4. $CH_3CH=CH.CH_2OH$
5. $CH_3CH_2CH=CHCH_3$
6. $CH_3CH=CH_2$ (A) ; $CH_3CHOHCH_3$ (B) ; CH_3COCH_3 (C)
7. $CH_3OH+HCOOK$
8. 
9. $CH_2ClCOONa$ (A) ; $CH_2CNCOONa$ (B) ;


$CH_2(COOH)_2$ (C) ;

$CH_2(COOC_2H_5)_2$ (D).

10. CH_3CHO (A) ; CH_3COOH (B) ; $CH_3COOC_2H_5$ (C).
11. CH_3CONH_2 (A) ; $CH_3C\equiv N$ (B) ; CH_3COOH (C).
12. $(CH_3COO)_2Ca$ (A)


$(CH_3)_2CO$ (B) ;

$(CH_3)_2C(OH)SO_3Na$ (C).

13. CH_3COOH (A) ; CH_3COCl (B) ; $(CH_3CO)_2O$ (C).
14. 
$CH_3CH(OH)CN$ (A) ;

$CH_3CH(NH_2)CN$ (B) ; $CH_3CHNH_2.COOH$ (C).

(D) MATCHING TEST TYPE :

1. Match the reagents in List A with the name reactions in List B.

A	(B)
(1) Metallic sodium	(*i*) Sabatier and Senderens reaction
(2) Magnesium	(*ii*) Williamson's synthesis
(3) Finely divided Ni	(*iii*) Stephen's reaction.
(4) I_2+NaOH	(*iv*) Rosenmund's reaction.
(5) RONa	(*v*) Clemmensen reaction.

(6) $Pd/BaSO_4$	(*vi*) Iodoform reaction.
(7) $SnCl_2+HCl$	(*vii*) Liebermann nitroso reaction.
(8) Zn/Hg+conc HCl	(*viii*) Cannizzaro reaction.
(9) HCHO+NaOH	(*ix*) Wurtz Synthesis.
(10) Phenol+conc H_2SO_4	(*x*) Tischenko reaction.
(11) Br_2+KOH	(*xi*) Meerwein Ponndorf reaction.
(12) P_4+Br_2	(*xii*) Kolbe's electrolytic reaction.
(13) $Al(OC_3H_7)_3$	(*xiii*) Aldol condensation.
	(*xiv*) HVZ reaction.
	(*xv*) Preparation of Grignard reagent.
	(*xvi*) Hofmann degradation.

2. Match the compounds in list A with their methods of preparation given in list B.

A	B
(1) Ethane	(*i*) Addition polymerisation of Vinyl chloride.
(2) Cyclopentanone	(*ii*) By catalytic combination of acetylene and chlorine.
(3) Propylene	(*iii*) Nitration of chloroform.
(4) Lewisite	(*iv*) Condensation polymerisation of methyl terephthalate and glycol.
(5) PVC	(*v*) By Wurtz synthesis from methyl chloride.
(6) Decron	(*vi*) Heating glycerol with oxalic acid at 530K.
(7) Chloropicrin	(*vii*) Heating glycerol with conc. H_2SO_4
(8) Westron	(*viii*) Acetone+conc. H_2SO_4.
(9) Allyl alcohol	(*ix*) Rosenmund's reaction.
(10) Acrolein	(*x*) By heating urea.
(11) Ether	(*xi*) $RCONH_2+Br_2+KOH$
(12) Aldehyde	(*xii*) Heating 2-propanol with conc. H_2SO_4.
(13) Biuret	(*xiii*) Heating calcium adipate.
(14) Maleic anhydride	(*xiv*) Williamson's synthesis.
(15) Mesitylene	(*xv*) Acetylene+$AsCl_3$.
(16) RNH_2	(*xvi*) Heating malic acid.

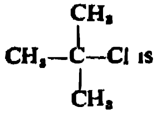
KEY

1. (1)—(*ix*) (2)—(*xv*) (3)—(*i*) (4)—(*vi*) (5)—(*ii*)
(6)—(*iv*) (7)—(*iii*) (8)—(*v*) (9)—(*viii*) (10)—(*vii*)
(11)—(*xvi*) (12)—(*xiv*) (13)—(*x*).

2. (1)—(*v*) (2)—(*xiii*) (3)—(*xii*) (4)—(*xv*) (5)—(*i*)
(6)—(*iv*) (7)—(*iii*) (8)—(*ii*) (9)—(*vi*) (10)—(*vii*)
(11)—(*xiv*) (12)—(*ix*) (13) (*x*) (14)—(*xvi*) (15)—(*viii*)
(16)—(*xi*).

(E) Selection Test Type :

Choose the correct alternative (s) out of the suggested ones as answer in the following questions :

1. (*i*)  $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Cl$ is

(*a*) 1°-butyl chloride (*b*) isobutyl chloride

(*c*) 2°-butyl chloride (*d*) 3°-butyl chloride

(*ii*) A strong solution of alcoholic alkali will preeferntially promote in an alkyl halide

(*a*) Substitution (*b*) Elimination

(*c*) Addition (*d*) Ionization

(*iii*) If two halogen atoms are attached to the same carbon atom of an alkane, it is termed as

(*a*) alkylene halide (*b*) alkylidene halide

(*c*) alkyl halide (*d*) 2-haloalkane]

(*iv*) An example of an electrophilic reagent is :

(*a*) $\overset{+}{N}O_2$ (*b*) OH^- (*c*) H_2O (*d*) $\cdot CH_3$

(*Osmania B.Sc. 1980*)

2 (*i*) Secondary alcohol on oxidation gives :

(*a*) ketone with less number of carbon atoms

(*b*) aldehyde

(*c*) ketone with same number of carbon atoms

(*ii*) The reaction product obtained when ethanol is passed over heated Al_2O_3, is :

(*a*) Ethylene (*b*) Acetylene (*c*) Ethane

(*Madras B.Sc. 1980*)

KEY

1. (*i*) —(*d*) (*ii*) —(*b*) (*iii*) —(*b*) (*iv*) —(*a*)

2. (*i*) —(*c*) (*ii*) —(*a*)

Textbook of Organic Chemistry

VOLUME TWO

Part III—Aromatic Compounds
Part IV—Polynuclear Hydrocarbons
Part V—Heterocyclic Compounds
Part VI—Special Topics—Carbohydrates, Proteins, Ureides, Alkaloids, Terpenoids, Biochemistry, Chemotherapy, Polymers, Colour and Dyes
Appendices—Typical Numerical Problems, Miscellaneous Questions, New Type Question Bank

"...The magnificent dyes colouring our garments and furnishings are derived from unsightly coal-tar [and]....sweet-tasting saccharin is prepared from the same material. The point is that chemical transformations are so thorough that the end product retains nothing at all of the properties of the original substance.. The manufacture of caffeine from uric acid is, therefore, nothing worse than the processes which occur when manure used to nourish plants is converted into appetizing fruits or into wonderfully scented flowers."

Emil Fischer (1902)

34

Introduction to Aromatic Compounds

1. **Aromatic Compounds.**—A large number of organic compounds obtained from natural sources, *e.g.*, resins and balsams, and having a pleasant odour are termed *aromatic* (Greek : *aroma*= fragrant smell). These contain higher percentage of carbon than the corresponding aliphatic compounds and contain at least six carbon atoms. *The term 'aromatic' is now reserved for benzene or compounds which resemble benzene in chemical behaviour.* These are closed chain or cyclic compounds. Their properties are, however, totally different from those of alicyclic compounds which resemble aliphatic compounds. Derivatives of benzenes are also termed *benzenoid compounds.*

Reasons for the Separate Classification of Aromatic Compounds. (*i*) Aromatic compounds are ring or closed-chain compounds whereas the aliphatic compounds have open-chain formulae. The ring structure confers on the aromatic compounds extreme stability in spite of their unsaturated nature.

(*ii*) They give nitro-derivatives when heated with concentrated nitric acid. In the case of aliphatic compounds the nitro-derivatives are not formed easily.

(*iii*) When heated with concentrated or fuming sulphuric acid, aromatic compounds undergo 'sulphonation' not common with aliphatic unsaturated compounds.

(*iv*) Aromatic amino-compounds are less basic than aliphatic amines.

(*v*) Hydroxy derivatives of aromatic compounds are acidic in nature whereas those of the corresponding aliphatic compounds are neutral towards litmus.

(*vi*) Aromatic halogen compounds are chemically much less active than the aliphatic compounds.

(*vii*) Aromatic compounds contain larger percentage of carbon than the aliphatic compounds.

(*viii*) A number of reactions given by aromatic compounds, *e.g.*, Friedel-Crafts reaction, Perkin's reaction and diazo reaction are not common in aliphatic compounds.

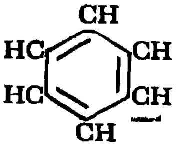
(*ix*) Aromatic hydrocarbons have a tendency to undergo ionic substitution. Aliphatic hydrocarbons, as we have seen, undergo chiefly addition at multiple bonds and free radical substitution at other points along the chain.

Undue weight should not, however, be attached to the distinction between aliphatic and aromatic compounds. For example, the similarities between aliphatic and aromatic amines or between aliphatic and aromatic acids are more important than the differences.

3. Nomenclature of Aromatic Compounds.—The names of homologous series and their particular members which we come across in the study of aromatic compounds are given below :

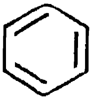
(*i*) **Hydrocarbons.** *General Formula* : C_nH_{2n-6}.

Members : Benzene, C_6H_6 is the first member. Here the six carbon atoms, each carrying one hydrogen atom, lie at the six corners of a regular hexagon and are joined to each other by alternate double and single bonds. Each one of the following formulae represents benzene :



(*i*)

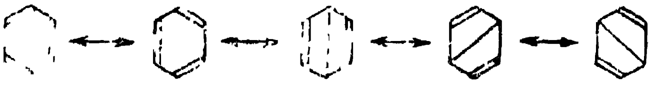
or



(*ii*)

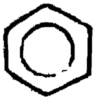
In formula (*ii*) the various carbon and hydrogen atoms are understood to be present.

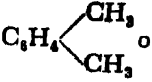
Benzene is considered to be a resonance hybrid of the following structures :



(*i*) (*ii*) (*iii*) (*iv*) (*v*)

Thus each single bond has some double bond character and all the six C—C bonds are equivalent. For convenience the hybrid structure of benzene is represented by a regular hexagon containing a circle.

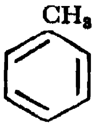
 means a hybrid of structures (*i*) to (*v*).

Toluene or methylbenzene, $C_6H_5.CH_3$ or C_7H_8 and *Xylene* or dimethylbenzene,  $C_6H_4\begin{matrix} \diagup CH_3 \\ \diagdown CH_3 \end{matrix}$ or C_8H_{10} are homologues of benzene.

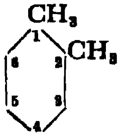
Structural representation of aromatic compounds. As recommended by the *Chemical Society*, benzenoid compounds should in general be represented by Kekule type structure. Large circles representing *six delocalised π electrons in cyclic systems* may, however, be used for certain types of compounds. The circles may be with or without positive or negative signs as required. Cyclic systems having less or more than six delocalised π-electrons may be represented by circles with broken lines.

Isomerism of Benzene Derivatives. Xylene shows *position isomerism* and the isomers are called *ortho*, *meta* or *para* according as the two methyl groups occupy adjacent, alternate or diagonal positions respectively in the *benzene nucleus* (benzene ring of six carbon atoms). Abbreviations *o*-, *m*-, and *p*- are used for ortho, meta and para, respectively.

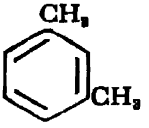
These are also named as dimethyl derivatives of benzene. The relative positions of the methyl groups are indicated by numbering the carbon atom as given below :



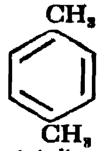
Methyl-benzene
or Toluene



1,2-dimethyl-benzene
or o-Xylene

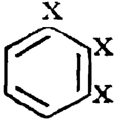


1,3-dimethyl-benzene
or m-Xylene

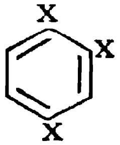


1,4-dimethyl-benzene
or p-Xylene

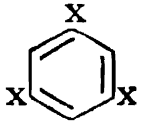
The tri-substitution products of benzene are termed *adjacent* or 1, 2, 3, *unsymmetrical* or 1, 2, 4 and *symmetrical* or 1, 3, 5 depending upon their relative positions as given below :



Adjacent
or 1, 2, 3



Unsymmetrical
or 1, 2, 4



Symmetrical
or 1, 3, 5

Nucleus and the side-chain. The six carbon atoms of the benzene ring constitute what is known as **nucleus**. Characteristic properties of the aromatic compounds are the properties of this nucleus.

An alkyl group or any other group containing one or more carbon atoms, when attached to the nucleus, is termed as the **side-chain**. Two methyl groups in xylene constitute two **side-chains** attached to the benzene nucleus. The side chain is aliphatic in character and gives reactions characteristic of aliphatic compounds.

Functional groups attached to the nucleus but not containing any carbon atom, *e.g.*, NH_2, NO_2, OH and Cl are not regarded as side-chains.

(*ii*) **Aryl Groups.** When the aromatic hydrocarbons lose one, two or three hydrogen atoms, *the mono-, di-, or trivalent residues left behind are called* **aryl groups** and are represented by the symbol Ar (*cf.* alkyl groups represented by R, on the aliphatic side).

Members :

C_6H_5- ;	$C_6H_5CH_2-$;	$C_6H_5CH<$;	$C_6H_5C\begin{smallmatrix}/\\-\\\backslash\end{smallmatrix}$	$C_6H_4<$
Phenyl (*Monovalent*)	Phenylmethyl or Benzyl (*Monovalent*)	Phenylmethylene or Benzylidene (*Divalent*)	Phenyl-methylidyne or Benzylidyne (*Trivalent*)	Phenylene (*Divalent*)

Phenyl is represented by abbreviation Ph or ϕ.

Isomeric with phenylmethyl or benzyl group, $C_6H_5CH_2$—(with one valency free in the side-chain) is the methylphenyl or tolyl radical, $CH_3.C_6H_4$—(with one valency free in the nucleus).

HOMOLOGOUS SERIES NAMED AFTER THE HYDROCARBONS OR ARYL GROUPS

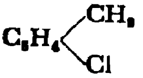
(*iii*) **Halogen Derivatives.** These are obtained by the replacement of one or more hydrogen atoms of the hydrocarbon by halogen atoms. The halogen atom may be present in the nucleus or in the side-chain. Aryl halides show position isomerism as usual.

***Members* :**

C_6H_5Cl ; Chlorobenzene or Phenyl chloride

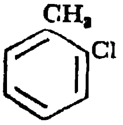
$C_6H_4Cl_2$; *o*-, *m*-, -and *p*-dichlorobenzene

$C_6H_3Cl_3$ Trichlorobenzene

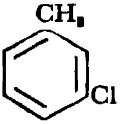


$C_6H_4\begin{cases}CH_3\\Cl\end{cases}$

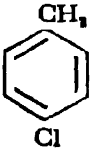
o-, *m*-, & *p*-Chlorotoluenes *or* Tolyl chloride



Ortho-



Meta-



Para-

(*Nuclear Substitution Products*)

$C_6H_5CH_2Cl$ Benzyl chloride

$C_6H_5CHCl_2$ Benzylidene chloride

$C_6H_5CCl_3$ Benzylidyne chloride

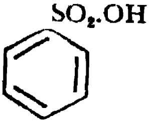
$C_6H_6Cl_6$ Benzene hexachloride

(*Side-chain substitution products*)

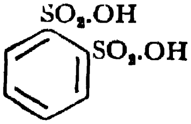
(*Addition cpd*)

(*iv*) **Sulphonic acids.** These are obtained by the replacement of one or more hydrogen atoms of the nucleus by sulphonic groups (—$SO_2.OH$).

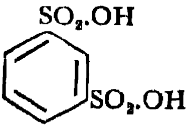
***Members* :**



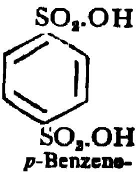
Benzene-sulphonic acid



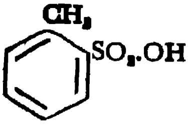
o-Benzene-disulphonic acid



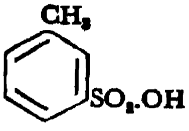
m-Benzene-disulphonic acid



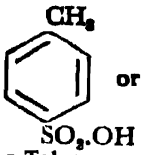
p-Benzene-disulphonic acid



o-Toluene-sulphonic acid

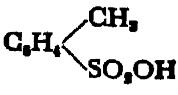


m-Toluene-sulphonic acid



p-Toluene-sulphonic acid

or



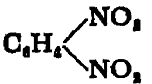
$C_6H_4\begin{cases}CH_3\\SO_3OH\end{cases}$

o-, *m*- & *p*-Toluene-sulphonic acids

(*v*) **Nitro-derivatives.** Aromatic nitro-compounds are obtained by replacement of one or more hydrogen atoms of the nucleus by a nitro group (—NO_2).

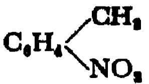
Members :

$C_6H_5NO_2$
Nitrobenzene



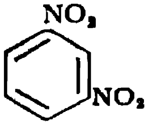
$C_6H_4{<}^{NO_2}_{NO_2}$

o-, *m-* & *p-*
dinitrobenzene

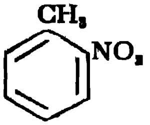


$C_6H_4{<}^{CH_3}_{NO_2}$

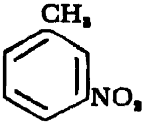
o-, *m-* & *p-*
nitrotoluenes



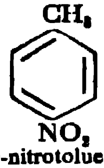
m-dinitro-
benzene



o-nitro-
toluene

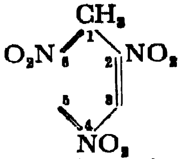


m-nitro-
toluene

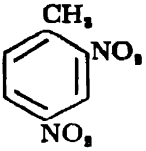


p-nitrotoluene

If more than two substituents are present in the nucleus, their positions are indicated by numbers. For example,



2,4,6-trinitrotoluene

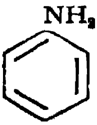


2,4-dinitrotoluene

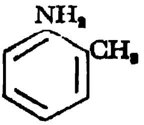
(*vi*) **Aromatic amines**. Aromatic amines are of two types, one in which the amino group is attached directly to the nucleus and the other in which the amino group is in the side-chain. The latter behave very much like the aliphatic amines, and so may be regarded as aryl substituted aliphatic amines.

Nuclear amino compounds may be primary amines, $ArNH_2$, secondary amines, Ar_2NH or tertiary amines, Ar_3N.

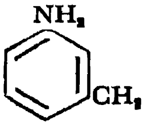
Particular Members :



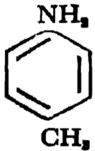
Phenylamine,
or benzeneamine
or aniline



2-Methyl-
benzeneamine
or *o*-toluidine

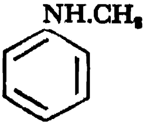


3-Methyl-
benzeneamine
or *m*-toluidine

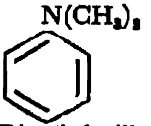


4-Methylbenzene-
amine
or *p*-toluidine

(Primary amino-compounds,—NH$_2$ attached to the nucleus)

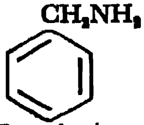


N-Methylaniline
(*Secondary*)



N,*N*-Dimethylaniline
(*Tertiary*)

(Nuclear amino compounds)



Benzylamine
(*Side-chain amino compound*)

(*vii*) Diazo compounds (Di=*two* ; **azo**=*nitrogen*). The **diazo** compounds contain the characteristic group, —N=N—.

***Members* :**

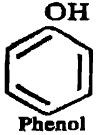
$C_6H_5—N{=}N—Cl$; $C_6H_5—N{=}N—OH$

Benzenediazonium chloride ; Benzenediazonium hydroxide

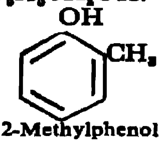
$C_6H_5.N{=}N.HSO_4$; $p.CH_3C_6H_4N{=}N.HSO_4$

Benzenediazonium sulphate ; *p*-Toluenediazonium sulphate

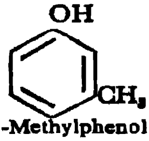
(*viii*) **Phenols* and Aromatic alcohols.** Nuclear hydroxy derivatives of hydrocarbons are called *phenols* whereas an —OH group when present in the side-chain gives an aromatic alcohol, *e.g.*, *benzyl alcohol*, $C_6H_5CH_2OH$.



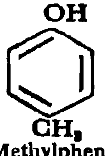
Phenol or Benzenol



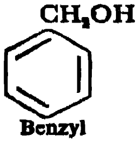
2-Methylphenol *or* 2-Methylbenzenol



3-Methylphenol *or* 3-Methylbenzenol



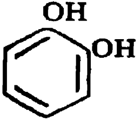
4-Methylphenol *or* 4-Methylbenzenol



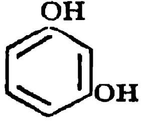
Benzyl alcohol *or* phenylmethanol

(Common names : *o*-, *m*- or *p*-cresols)

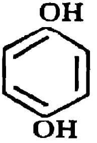
Three dihydric phenols, *o*-, *m*-, and *p*-dihydroxybenzenes, are :



1, 2-Benzenediol *not* catechol

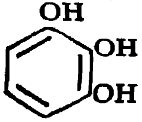


1, 3-Benzenediol *not* resorcinol

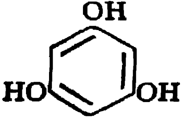


1, 4-Benzenediol *not* quinol

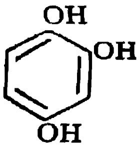
Three trihydroxybenzenes or trihydric phenols are :



1, 2, 3-Benzenetriol *not* pyrogallol



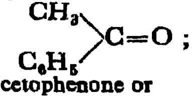
1,3,5-Benzenetriol *not* phloroglucinol



1, 2, 4-Benzenetriol *not* hydroxyquinol

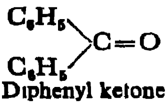
(*ix*) **Aromatic Ketones.** The characteristic group of aromatic ketones is $\gt C{=}O$ and these are named after the aryl or alkyl groups attached (*cf.*, aliphatic ketones).

Members :



$$\begin{matrix} CH_3 \\ C_6H_5 \end{matrix} \gt C{=}O$$

Acetophenone or Methyl phenyl ketone



$$\begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix} \gt C{=}O$$

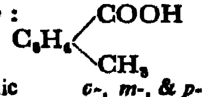
Diphenyl ketone or Benzophenone

(*x*) **Aromatic acids.** Just like aliphatic acids the aromatic acids contain one or more characteristic —COOH groups attached to the benzene nucleus or side-chain.

Members :

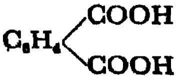
C_6H_5COOH

Benzoic acid *or* Benzenecarboxylic acid



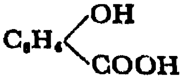
$$C_6H_4 \begin{matrix} COOH \\ CH_3 \end{matrix}$$

o-, *m*-, & *p*-toluic acids *or* 2, 3, & 4-Methylbenzoic acids



$$C_6H_4 \begin{matrix} COOH \\ COOH \end{matrix}$$

o-, *m*-, & *p*-benzenedicarboxylic acids



$$C_6H_4 \begin{matrix} OH \\ COOH \end{matrix}$$

o-, *m*-, & *p*-hydroxybenzoic acids

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*The common names cresol, catechol, resorcinol, quinol, pyrogallol, phloroglucinol and hydroxyquinol are not recommended in IUPAC system and should not be used.

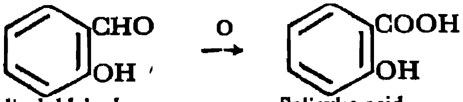
HOMOLOGOUS SERIES NAMED AFTER THE ACIDS

(*xi*) **Aromatic Aldehydes.** The characteristic group of aldehydes is —CHO and these are named after the acid which they give on oxidation (*cf.*, aliphatic aldehydes).

Members :

$$C_6H_5CH{=}O \xrightarrow{O} C_6H_5COOH$$

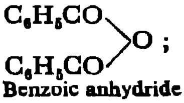
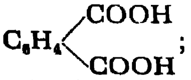
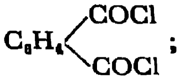
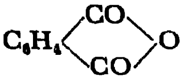
Benzaldehyde or Benzene-carbaldehyde	Benzoic acid or Benzenecarboxylic acid



Salicylaldehyde (*o*-hydroxybenzaldehyde)	Salicylic acid (*o*-hydroxybenzoic acid)

(*xii*) **Acid chlorides (Aroyl chlorides), amides and anhydrides.** The acid derivatives are similar to those given on the aliphatic side.

Members :

Parent acid	*Acid derivatives*		
C_6H_5COOH Benzoic acid	C_6H_5COCl : Benzoyl chloride	$C_6H_5CONH_2$; Benzamide *or* Benzene-carboxamide	 $\begin{matrix}C_6H_5CO\\C_6H_5CO\end{matrix}\!\!>O$; Benzoic anhydride
 $C_6H_4\left\langle\begin{matrix}COOH\\COOH\end{matrix}\right.$; Phthalic acid	 $C_6H_4\left\langle\begin{matrix}COCl\\COCl\end{matrix}\right.$; Phthalyl chloride or Phthaloyl chloride	 $C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle O$ Phthalic anhydride	

Points to Remember about Nomenclature of Benzene Derivatives

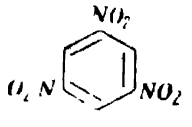
(1) Some aromatic compounds are named as substituted benzenes, *e.g.*, chlorobenzene, bromobenzene, nitrobenzene, etc. In these benzene is the base name and the substituent is indicated by a prefix.

(2) In some other compounds the substituent along with the benzene ring are given a new base name. For example, methylbenzene ($C_6H_5CH_3$) is called toluene. Similarly, hydroxybenzene (C_6H_5OH) is termed phenol and aminobenzene ($C_6H_5NH_2$) is known as aniline. Some other names of this kind are :

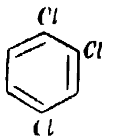
C_6H_5COOH	$C_6H_5SO_3H$	$C_6H_5COCH_3$
Benzoic acid	Benzenesulphonic acid	Acetophenone

(3) When two substituents are present in the ring, their relative positions are indicated by use of the prefixes ortho, meta and para.

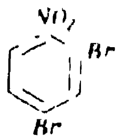
(4) If more than two substituents are present in the benzene ring, their relative positions are indicated by the use of numbers. *Carbon atoms of the benzene ring are so numbered as to give the lowest possible numbers to the substituents.* For example,



1,3,5-Trinitro-
benzene



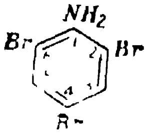
1,2,4-Trichlorobenzene
(not 1,3,4-Trichlorobenzene)



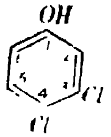
2,4-Dibromo-
1-nitrobenzene

Substituents are usually listed in alphabetical order as in the last example given above.

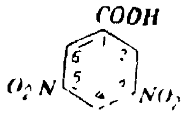
(5) In the case of a substituent, X which when taken together with benzene ring has a separate base name, carbon atom bearing X is numbered 1- and the compound named accordingly. For example,



2,4,6-Tribromo-
aniline

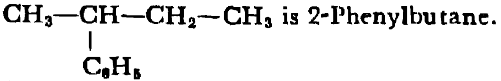


3,4-Dichloro-
phenol



3,5-Dinitro-
benzoic acid

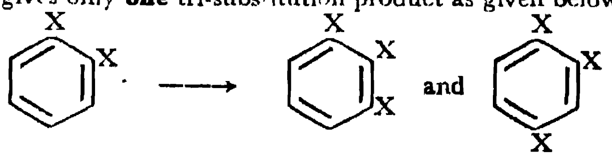
(6) In C_6H_5—R, if R contains more carbon atoms, it is named as phenyl substituted alkane. For example,



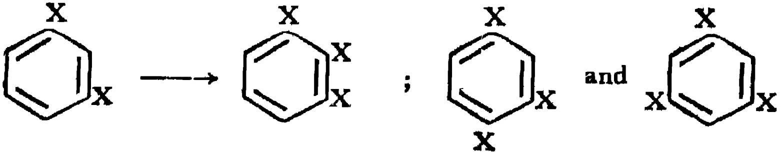
$$\underset{\displaystyle C_6H_5}{CH_3-\underset{|}{CH}}-CH_2-CH_3 \text{ is 2-Phenylbutane.}$$

4. **Orientation.**—*The process of finding the relative positions of various groups attached to the nucleus in an unknown derivative is termed* **Orientation.** For example, if we are given a sample of xylene, then to find out whether it is ortho, meta- or para-xylene, is orientation. Three methods generally employed for the purpose are :

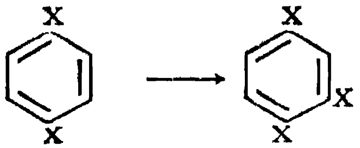
(1) **Korner's Absolute Method.** When a di-substituted substance is converted into a tri-substituted product then **ortho**-derivative gives **two**, the **meta**-derivative gives **three** while the **para**-derivative gives only **one** tri-substitution product as given below :



Ortho *1, 2, 3* *1, 2, 4*
(*Two tri-derivatives*)



Meta *1, 2, 3* *1, 2, 4* *1, 3, 5*
(*Three tri-derivatives*)



Para *1, 2, 4*

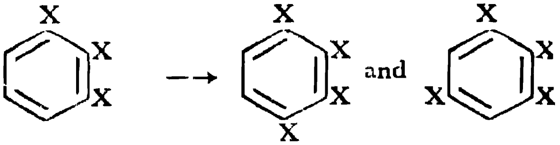
(One tri-derivative)

Hence for orientation :

(*i*) *Convert the di-substituted substance Y into a tri-substitution product and analyse the product Z obtained.*

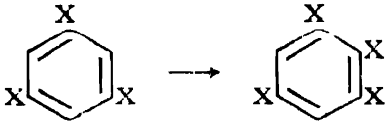
(*ii*) *If Z is a single substance, Y is a para-derivative ; if Z is a mixture of two substances, Y is an ortho-derivative while if Z is a mixture of three substances, Y is a meta-derivative.*

Similarly, when a tri-substituted substance is converted into a tetra-substitution product, the number of derivatives obtained are :



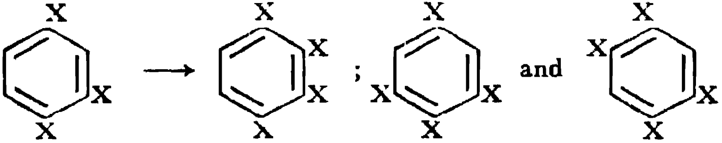
1, 2, 3 *1, 2, 3, 4* *1, 2, 3, 5*

(Adjacent) *(Two tetra-derivatives)*



1, 3, 5 *1, 2, 3, 5*

(Symmetric) *(Only one tetra-derivative)*



1, 2, 4 *1, 2, 3, 4* *1, 2, 3, 5* *1, 2, 4, 5*

(Unsymmetric) *(Three tetra-derivatives)*

Hence for orientation :

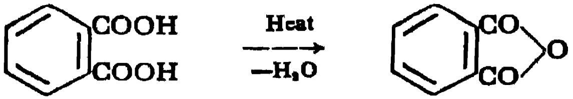
(*i*) *Convert the tri-derivative Y into a tetra-derivative and analyse the product Z obtained.*

(*ii*) *If Z is a single substance, Y is the 1, 3, 5 (symmetric) derivative ; if Z is a mixture of two substances, Y is 1, 2, 3 (adjacent) derivative and when Z is a mixture of three substances, Y is 1, 2, 4 (unsymmetric) derivative.*

In practice Korner's method of orientation is often difficult, if not impossible, since all the products cannot always be isolated due to the fact that some are formed in very small amounts.

(2) **The Relative Method.** In this method the relative position of the substituents in an unknown compound is determined indirectly by studying its properties. Alternatively, the compound under examination is converted into or synthesised from another compound *of previously known orientation.* For example :

(*a*) *By studying its reactions.* Three benzenedicarboxylic acids are known. These are phthalic acid, isophthalic acid and terephthalic acid. Out of these the first gives an anhydride on heating. This must obviously be the ortho-isomer in which the two carboxyl groups, being in close proximity, eliminate a molecule of water.

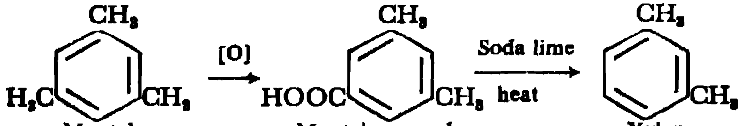


Phthalic acid Phthalic anhydride

(*b*) *By synthesising it from another compound of previously known orientation.* Three isomeric xylenes are known. Out of these the one with a boiling point 412K, can be obtained from mesitylene as follows :

$$\text{Mesitylene} \xrightarrow[\text{oxidation}]{\text{Partial}} \text{Mesitylenic acid} \xrightarrow[\text{soda lime}]{\text{Heat with}} \text{Xylene (b.p.}=412\text{K)}$$

Since three methyl groups in mesitylene are in meta position to one another, removal of one of them must have left the remaining two in meta position. Thus xylene boiling at 412K is *m*-xylene.



Mesitylene Mesitylenic acid *m*-Xylene

(*c*) *By converting it into another compound of previously known orientation.* One of the xylenes, which boils at 417K, gives on oxidation phthalic acid which yields phthalic anhydride on heating. Obviously in phthalic acid the two —COOH groups are in ortho position. The two —CH_3 groups in this xylene must, therefore, be present in ortho position.

Thus out of the three unknown xylenes the one (b.p. 412K) is meta, the second (b.p. 417K) is ortho and the third (b.p. 411K), therefore, is para.

This method is based on the assumption that atoms or groups remain in the same position or exchange position with the in-coming groups. Sometimes, however, this assumption is not correct in practice.

(3) **Dipole Measurements Method.** In certain cases where the two substituents are either atoms or simple groups, measurement of dipole moment of the compound helps in the orientation. For example, the observed dipole moment of C—Cl bond (in chlorobenzene) is 1·55D. By using this value we can calculate* the dipole

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* Making use of the law of ||ᵐ of forces, $R^2=P^2+Q^2+2PQ\cos\theta$, we get for ortho derivative

$R^2=1{\cdot}55^2+1{\cdot}55^2+2\times1{\cdot}55\times1{\cdot}55\ \cos\ 60(=\frac{1}{2})=1{\cdot}55^2(1+1+2\times\frac{1}{2})=1{\cdot}55^2\times3$

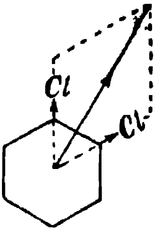
whence $R=1{\cdot}55\times\sqrt{3}=2{\cdot}68$

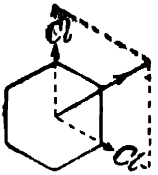
For meta deriv., $\theta=120°$

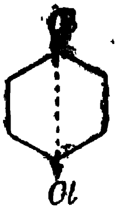
$\therefore R^2=1{\cdot}55^2+1{\cdot}55^2+2\times1{\cdot}55\times1{\cdot}55\ \cos\ 120(=-\frac{1}{2})=1{\cdot}55^2(1+1-1)=1{\cdot}55^2$

whence $R=1{\cdot}55.$

moments of three dichlorobenzenes (*o*-, *m*-, and *p*-). By comparing the calculated values with the observed ones, we can decide the orientation of the given dichlorobenzene.



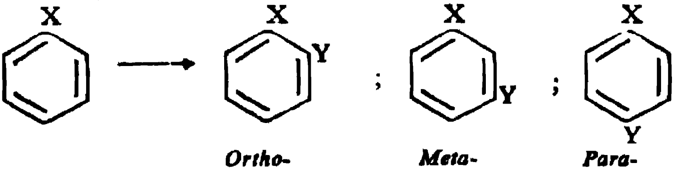




Dipole moment :

	Ortho-	*Meta-*	*Para-*
Calculated :	2·68D	1·55D	0
Observed :	2·30D	1·48D	0

5. Substitution in the Benzene Ring.—When one group X is introduced into the benzene nucleus, only one product is obtained. When, however, a second group, Y is introduced, three isomeric di-substitution products are possible.



Experiments have shown that *the main product is either a mixture of o- and p-isomers* (*m*-isomer being comparatively in smaller quantity) *or it is m-isomer* (*o*- and *p*-isomers being comparatively in smaller quantity). *Also the rate of o- and p-substitution is very much greater than that of m*-substitution, *e.g.*, bromination of phenol to *s*-tribromophenol is extremely rapid but that of nitrobenzene is slow.

6. Directive Influence of Groups.—Experience has shown that the nature of group X already present in the nucleus determines the position taken by the in-coming group.

Various groups have been sub-divided into two distinct classes :

Class I—Those which direct the in-coming group to the ortho and para position. Different *o*- and *p*-directing groups are : R, OH, SH, OR, NH_2, NHR, NR_2, $NHCOCH_3$, Cl, Br, I, CH_2Cl, C_6H_5, etc.

Class II—Those which direct the in-coming group to the m-position. Different *m*-directing groups are : NO_2, CHO, COOH, COOR, $COCH_3$, SO_3H, SO_2Cl, CN, CCl_3, etc.

Considerable work has been done in determining the preferential orienting effect of groups. Percentages of ortho-, meta- and para-substitution products obtained on mononitration of various mono-substituted benzenes are given in the table on the next page.

Substituent	% Ortho	% Meta	% Para
$—OH$	40	—	60
$—F$	12	0·5	87
$—Cl$	29·6	0·9	69·5
$—Br$	36·5	1·2	62·3
$—I$	37·9	2·1	60
$—CH_3$	58·5	4·4	37·1
$—CH_2CH_3$	43	6·5	48·5
$—CH(CH_3)_2$	30	7·7	62·3
$—C(CH_3)_3$	15·8	11·5	72·7
$—CH_2COOEt$	42	10·6	47·4
$—CH_2Cl$	32	15·3	52·5
$—CHCl_2$	23·3	33·8	42·9
$—CCl_3$	6·8	64·5	28·7
$—COOEt$	24	72	4
$—COOH$	18·5	80·2	1·3
$—CN$	17	81	(2)
$-CH_2\overset{+}{N}(CH_3)_3$	2	88	10
$—NO_2$	6·4	93·3	0·3
$—\overset{+}{N}(CH_3)_3$	—	100	—

It can be seen from above that very few groups lead to all *ortho*- and *para*- substitution or all *meta*-substitution. A substituent which gives 40% or more *meta*-isomer is classified as *m*-directing group.

In addition to the nature of the group already present in the nucleus which determines orientation some other factors also play some part. For example, *spatial size of the entering group* as illustrated by the orientation for monoalkylation of toluene is given in the table below :

Entering Group	% *o*-substitution	% *m*-substitution	% *p*-substitution
$—CH_3$	53·8	17·3	28·8
$—CH_2.CH_3$	45	30	25
$—CH(CH_3)_2$	37·5	29·8	32·7
$—C(CH_3)_3$	0	7	93

It is seen *that as the size of the entering group increases, the amount of ortho-isomer obtained decreases.* This is due to the spatial barrier preventing the reagent from approaching the substituent of *ortho*-substitution.

A similar steric effect is noticed when the size of the alkyl group already present in the ring increases. As illustrated by mononitration of alkylbenzenes, the amount of *ortho*-isomer obtained decreases as the size of alkyl group increases.

Compound	%*o*-isomer	%*m*-isomer	%*p*-isomer
$C_6H_5CH_3$	58·5	4·4	37·1
$C_6H_5C_2H_5$	45	6·5	48·5
$C_6H_5CH(CH_3)_2$	30	7·7	52·3
$C_6H_5C(CH_3)_3$	15·8	11·5	72·7

Even the nature of the attacking reagent affects the orientation observed. For example, *m*-isomer obtained on halogenation of toluene is less than 5%, on nitration it is 4%, while on alkylation it is up to 30%.

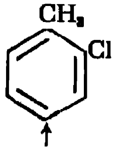
In spite of these second-order effects the nature of the group already present in the nucleus determines the position taken by the in-coming group.

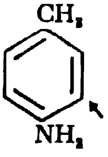
7. **Introduction of a Third Group into the Benzene Ring.**—The position occupied by a third group entering the benzene ring is determined by the nature of the two groups already present there.

(*i*) When both the groups belong to class I, the directive influence of each group is in the following order :

$$O^- > NR_2 \triangleright NH_2 > OH > OMe,\ NHCOCH_3 > CH_3 \triangleright X$$

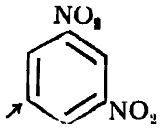
Out of ortho- and para-positions the new group enters *p*-position preferably, *i.e.*, more of *p*-isomer is formed than the *o*-isomer. For example, in *o*-chlorotoluene —CH_3 is more powerful than —Cl and the third group enters a position para to CH_3 (indicated by arrow). In *p*-toluidine, —NH_2 is more powerful than —CH_3, the new entrant is directed in *o*-position (indicated by arrow) to —NH_2, the *p*-position being blocked.





(*ii*) When both the groups belong to class II, the third group is introduced only with difficulty. The directive influence of each group is in the following order :

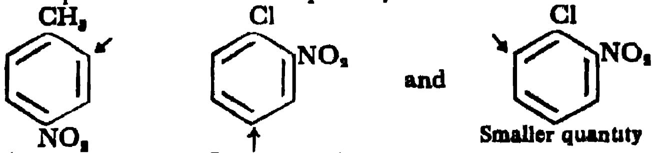
$$Me_3N^+ > NO_2 > CN > SO_3H > CHO > COMe > COOH$$



For example, in *m*-dinitrobenzene the third group comes in the position which is meta to both.

(*iii*) When the two groups exert different directive influences the group belonging to class I takes precedence. In case the influences of two groups reinforce each other, the third group enters almost entirely in one position. For example, in *p*-nitrotoluene the third group enters almost entirely in a position *ortho* to CH_3 and *meta* to

NO_2 group. In the case of *o*-nitrochlorobenzene two isomeric tri-substitution products are obtained. In one case new group enters in the position *meta* to NO_2 and *para* to Cl. This position is preferred. In the other case new group enters the position *meta* to NO_2 and *ortho* to Cl. This product is smaller in quantity.



Only one product Larger quantity Smaller quantity

(*Two isomers*)

(*Position occupied by newly-entering group is indicated by arrowhead.*)

8. Separation of Isomers.—We have seen that a mixture of ortho and para isomers is always obtained from which the individual isomers have to be separated. Three methods commonly used for the purpose are :

(*i*) *Steam distillation.* *Ortho*-isomer is sometimes steam-volatile and *para*- is not. The two can thus be easily separated by steam distillation.

(*ii*) *By freezing.* The boiling points being very close to each other, the isomers cannot be separated by fractional distillation. Their melting points are, however, usually different. Melting point of *p*-isomer being much higher than that of *o*-isomer, the mixture is cooled, if necessary, to get the *p*-isomer in the solid form and separated by filtration.

(*iii*) *Chemical methods.* In certain cases the isomers are separated by chemical methods.

9. Effect of Substituents : Reactivity and Orientation.—A group is classified as *activating* if the ring it is attached to is more reactive than benzene, and is classified as *deactivating* if the ring it is attached to is less reactive than benzene. The reactivities of benzene and a substituted benzene are compared in one of the following ways :

(*i*) *By comparing times required for reaction to occur under identical conditions.* Times required for sulphonation of toluene and benzene with fuming sulphuric acid are in the ratio 1 : 10. Toluene is, therefore, more reactive than benzene and $—CH_3$ is an activating group.

(*ii*) *From the severity of conditions required for the comparable reactions.* Benzene is nitrated in less than an hour at 330K when treated with conc. H_2SO_4+conc. HNO_3 mixture. Nitrobenzene gives dinitrobenzene only when treated with fuming nitric acid and conc. H_2SO_4 mixture at 360K. Nitrobenzene is evidently less reactive than benzene and $—NO_2$ group is a deactivating group.

(*iii*) *By carrying competitive reactions under identical reaction conditions.* Equimolar amounts of benzene and toluene are treated with small amount of conc. HNO_3 in nitromethane (a solvent which dissolves both reactants). The products nitrotoluene and nitrobenzene are formed in the ratio 25 : 1. This shows that toluene is 25 times more reactive than benzene and $—CH_3$ is an activating group.

On the other hand, nitration of a mixture of equimolar amounts of benzene and chlorobenzene with small quantity of conc. HNO_3 yields a product in which nitrobenzene and nitrochlorobenzene are in the ratio 30 : 1. This shows that benzene is 30 times more reactive than chlorobenzene and —Cl is a deactivating group.

It will be interesting to note that all these activating groups are *electron-releasing groups* (*i.e., act as electron source*) and are *o*- and *p*-directors whereas the deactivating groups are *electron-withdrawing groups* (*i.e., act as electron sink*) and are *m*-directors. Hence in general we can remember—**Electron-releasing groups are ortho- and para-directors whereas Electron-withdrawing groups are meta-directors.**

Nearly all groups fall into one or the other of the two classes : (*i*) activating and *o*- and *p*-directing, and (*ii*) deactivating and *m*-directing. The halogens are a class by themselves being deactivating and *o*- and *p*-directing.

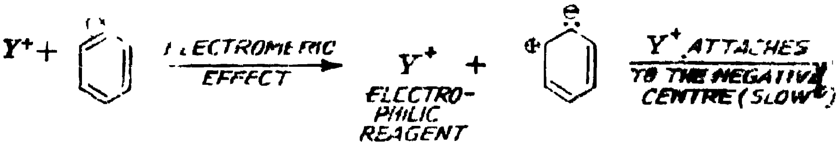
Knowing the class to which a group belongs, we can predict fairly accurately the course of the aromatic substitution. For example, bromination of nitrobenzene will be slower than bromination of benzene whereas nitration of acetanilide will be more rapid than nitration of benzene.

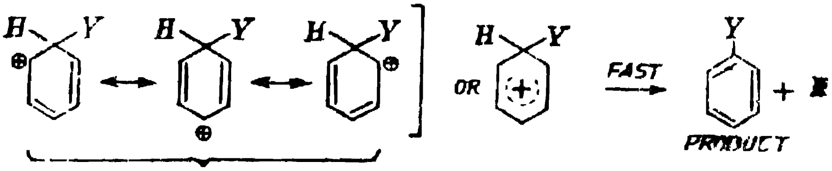
Table 34·1—Common Aromatic Substituents in the approximate order of decreasing electron-release (increasing electron-withdrawal)

Type of Substituents	Substituent	Effect
$-\ddot{Z}$ **(Key atom has a lone pair of electrons)**	$-\ddot{\underset{..}{O}}:^-$ $-\ddot{N}R_2$ $-\ddot{N}H_2$ $-\ddot{\underset{..}{O}}H$ $-\ddot{\underset{..}{O}}R$ $-\ddot{O}\overset{O}{\overset{\|}{C}}R,\ -\ddot{N}H.\overset{O}{\overset{\|}{C}}R$	
Not classified by structure	$-R,\ -\underset{..}{C}H{=}CH_2$	↑ **activating** ***o*-, *p*-directing**
$-\ddot{Z}$	$-\ddot{\underset{..}{Cl}}:,\quad -\ddot{\underset{..}{Br}}:,\quad -\ddot{\underset{..}{I}}:$	**deactivating** ***o*-, *p*-directing**
$-X^{\diagup Y}$ **(Wherein Y is more electronegative than X)**	$-\overset{O}{\overset{\|}{C}}OH$ $-\overset{O}{\overset{\|}{C}}R,\quad -\overset{O}{\overset{\|}{C}}H$ $-SO_3H$ $-C{\equiv}N$ $-\overset{+}{N}{\genfrac{}{}{0pt}{}{\diagup O}{\diagdown O^-}}$	↓ **deactivating** ***m*-directing**

10. Mechanism of Aromatic Substitution.—There are three possible mechanisms for aromatic substitution : (*i*) Electrophilic, (*ii*) Nucleophilic, and (*iii*) Free radical mechanism. Common substitution reactions, however, involve electrophilic reagents. We shall discuss briefly electrophilic mechanisms.

(A) **Electrophilic substitution.** Electrophilic aromatic substitution is believed to proceed by a bimolecular (S_E2) mechanism involving *the formation of an intermediate** (σ complex) which is a rate determining step. This can be summarized for the reagent YZ as follows :



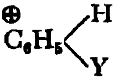


σ Complex (a resonance hybrid)

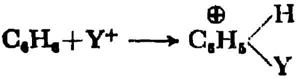
Note. As the electrophile approaches the benzene ring, an electromeric effect takes place with the result that one carbon atom of the benzene ring gets positively charged and the other gets negatively charged. The electrophile attaches to the negative centre resulting in the formation of a carbocation (an arenium ion). The polarisation of this double bond of benzene and the electrophilic attack are simultaneous and there is no time-lag between the two processes. The two steps given above are only there to clarify the idea.

Two essential steps involved in electrophilic substitution are :

(1) Attack by the electrophilic reagent Y^+ upon the ring to form a carbocation,

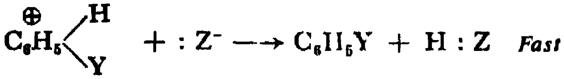


$\overset{\oplus}{C_6H_5}\langle^{H}_{Y}$



$$C_6H_6 + Y^+ \longrightarrow \overset{\oplus}{C_6H_5}\langle^{H}_{Y} \qquad \textit{Slow}$$

(2) Abstraction of a proton from the carbocation by some base (: Z^- here).



$$\overset{\oplus}{C_6H_5}\langle^{H}_{Y} + :Z^- \longrightarrow C_6H_5Y + H:Z \qquad \textit{Fast}$$

In each case there is a preliminary acid-base reaction which generates the attacking particle, Y^+. The actual substitution, however, is contained in these two steps.

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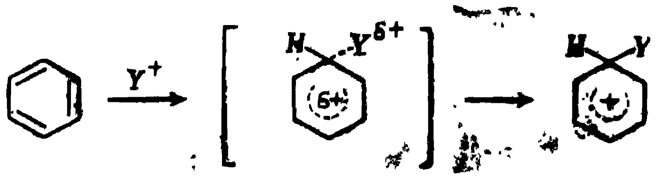
*Formation of the intermediate, being slow, is the rate-determining step.



Transition state : *developing positive charge*

Carbocation or σ complex : *full positive charge*

The σ complex is a true intermediate in various electrophilic substitution reactions. It is not a transition state. In a potential energy diagram the σ complex lies in a valley situated between two transition states involved in the substitution reaction (Fig. 34·1).

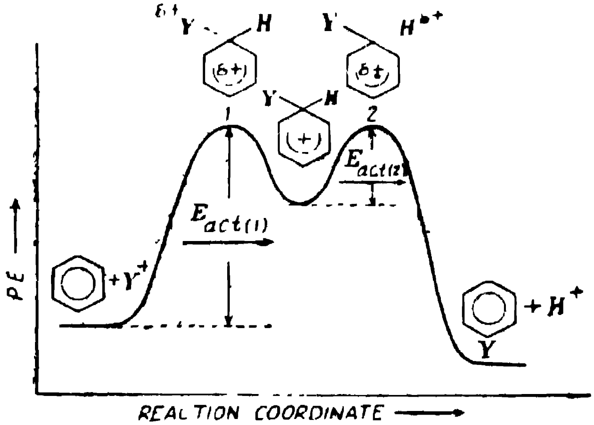


Fig. 34·1—Potential energy diagram for an electrophilic aromatic substitution reaction. σ complex lies in the valley between the two transition states (T.S.) 1 and 2.

In the T.S. 1 the electrophile Y^+ has as yet only partially attached to the benzene ring.

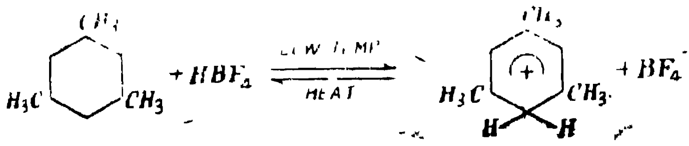
In the T.S. 2 the bond between the carbon atom and the proton is only partially broken.

The energy of activation for the formation of σ complex from benzene and the electrophile Y^+ $\underset{\longrightarrow}{E_{act\,(1)}}$ has been found to be much larger than the energy of activation $(\underset{\longrightarrow}{E_{act\,(2)}}$ for the formation of substituted benzene from σ complex.

This is because formation of σ complex is highly endothermic since in this change benzene ring loses its resonance energy.

On the other hand, decomposition of σ complex to give substituted benzene is by contrast highly exothermic because in this change the benzene ring regains its resonance energy.

An evidence in support of this is the actual separation of σ complex on treating mesitylene with fluoboric acid, HBF_4 at low temperatures. Here the electrophile is a proton.

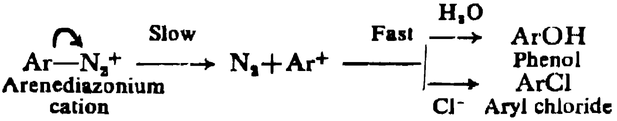


Mesitylene σ complex

σ complex can be isolated as a bright yellow ionic solid which decomposes on heating to regenerate mesitylene.

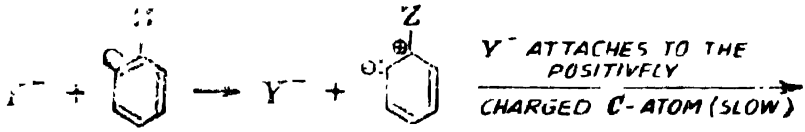
(B) **Nucleophilic substitution.** Replacement of hydrogen or any other substituent by a nucleophilic reagent is termed *nucleophilic substitution.* This replacement when facilitated by the presence of an electron-withdrawing group in the *o*- and/or the *p*-position, is termed *activated nucleophilic aromatic substitution.* The substitution is mainly of two types—*unimolecular* (S_N1) and *bimolecular* (S_N2).

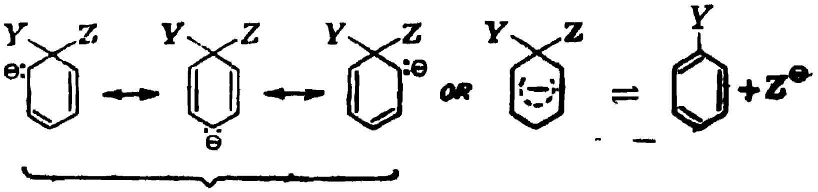
Unimolecular substitution. This mechanism is most uncommon in aromatic substitution. Decomposition of arenediazonium cations in aqueous solution to yield phenol or aryl halides (in presence of nucleophilic halide ions) are only well-established example of unimolecular nucleophilic substitutions.



$$\underset{\text{Arenediazonium cation}}{\mathrm{Ar{-}N_2^+}} \xrightarrow{\text{Slow}} \mathrm{N_2+Ar^+} \xrightarrow{\text{Fast}} \begin{cases} \xrightarrow{\mathrm{H_2O}} \underset{\text{Phenol}}{\mathrm{ArOH}} \\ \xrightarrow[\mathrm{Cl^-}]{} \underset{\text{Aryl chloride}}{\mathrm{ArCl}} \end{cases}$$

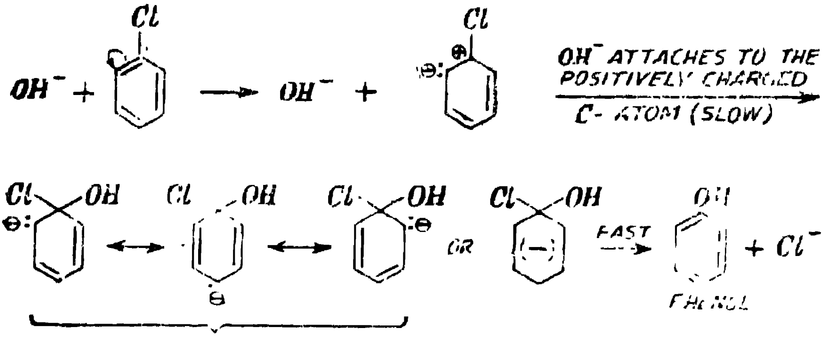
Bimolecular substitution. Nucleophilic aromatic substitutions are commonly bimolecular and proceed through a negative ion intermediate as shown below :





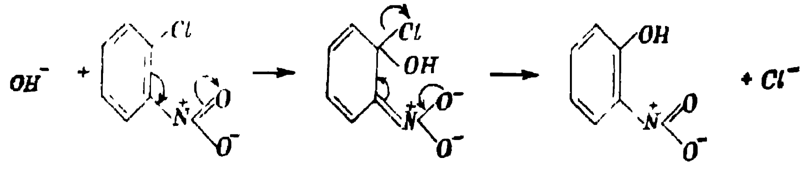
Resonating structures of the benzenonium carbanion (or cyclohexadienyl anion) intermediate.

Preparation of phenol by the action of 10% NaOH solution on chlorobenzene under pressure at 570K is a bimolecular nucleophilic substitution (S_N2) and may be represented as follows :



Resonating structures of the cyclohexadienyl anion intermediate.

An example of activated nucleophilic substitution (bimolecular) is the conversion of *o*-chloronitrobenzene into *o*-nitrophenol by heating with aqueous sodium hydroxide at 470K as represented below :



o-chloronitrobenzene Negative ion intermediate *o*-nitrophenol

In *o*-chloronitrobenzene, because of the electron-withdrawing effect of the nitro group, the carbon atom of the C—Cl group acquires a positive charge. Negatively charged OH⁻ attacks this positively charged carbon atom of the C—Cl group.

11. Reactivity and Orientation.—We have seen that certain groups activate the benzene ring and direct substituents to *ortho* and *para* positions and that some others deactivate the ring and direct substituents to *meta* position. Let us account for these effects.

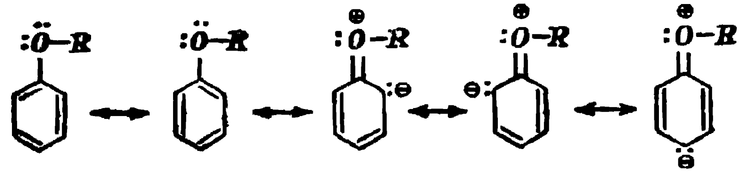
Reactivity and orientation are both matters of relative rates of reaction. Methyl group is said to activate the ring because it makes the ring react *faster* than benzene. It causes *ortho*, *para* orientation because it makes these positions react faster than *meta* positions.

There are two ways of studying the effect of substituents in electrophilic substitution. One is based on charge distribution and the other is based on the stabilities of the intermediate carbocations (σ-complexes). In both these approaches the effects given hold good for kinetically-controlled products and not necessarily for thermodynamically-controlled products.

(1) **Reactivity and Orientation based on charge distribution**. The polar effect (I and/or R) of the substituent **Y** present in the benzene ring results in charge distribution. ***In o-p-substitutions group Y causes these positions to become points of***

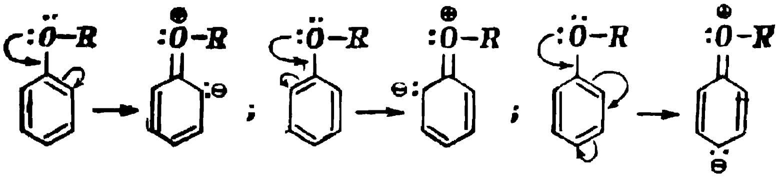
high electron density by inductive, electromeric and resonance (mesomeric) effects. Further substitution by electrophilic groups occurs at these points. Overall electron density of the ring also increases and further substitution is facilitated.

Groups OH, OR, NH_2, etc., are all *o- p*-directing. In all these *groups, the* atom adjacent *to the* nucleus—the "key atom"—has at least one lone pair of electrons. Resonance effect when Y=OR is shown as follows :



C_6H_5OR is a resonance hybrid of structure, I—V.

The mesomeric effect results in electronic displacement away from group OR (+M effect). In addition to this +M effect, the electromeric (+E) effect will be brought into play as under :

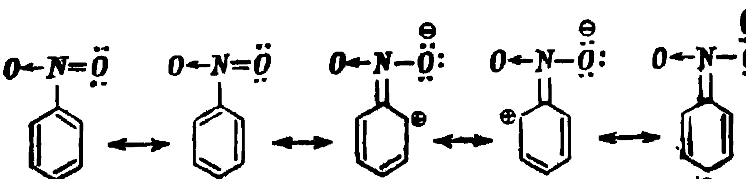


It, therefore, follows that *o- p*-substitution takes place by the combined mesomeric and electromeric effects. The combined effect is known as the *conjugative effect* or *tautomeric effect* (±T).

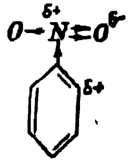
***In meta-substitution,* group Y causes a withdrawal of electrons from *o-* and *p*-positions (*i.e.*, —M effect). Thus *m*-position becomes a point of relatively high electron density and further substitution by electrophilic groups occurs here. Since overall electron density of the ring decreases, further substitution is difficult.**

Groups NO_2, COOH, COR, SO_3H, etc., are all *m*-directing.

Resonance effect when Y=NO_2 is shown as follows :



$C_6H_5NO_2$ is a resonance hybrid of structures I—V. Due to mesomeric effect there is withdrawal of electrons from the *o*- *p*-positions which results in deactivating the ring. Furthermore, since these *m*-directing groups contain at least one strongly electron-attracting atom, the inductive effect of this atom also helps to withdraw electrons from the *o*- and *p*-positions as shown on the right for nitrobenzene.



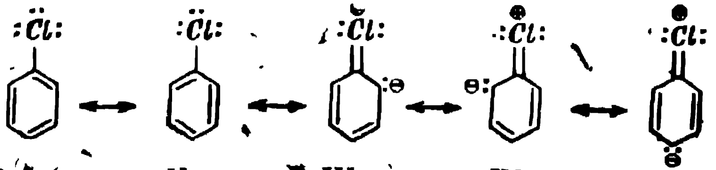
Nitrobenzene.

Here oxygen atom is strongly electron-attracting atom and causes inductive effect.

Thus in this case the mesomeric (—M), and inductive (—I) effects all assist one another and the net result is (—M—I).

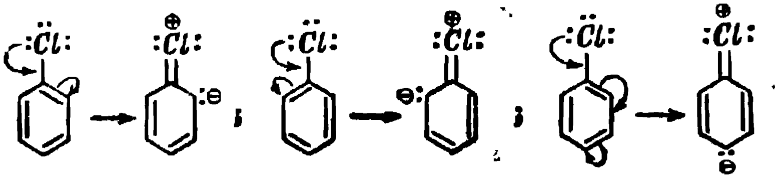
Since an electrophile requires a +E electromeric effect, this opposes the —M effect. However, the +E effect is very weak or is absent.

Groups Cl, OH, NH_2, etc., have a strong —I effect and hence tend to withdraw electrons from the ring to promote *m*-substitution. The 'key atom' in these groups, however, has at least one lone pair of electrons and hence both mesomeric and electromeric effects are possible as shown below :



I II III IV V

Chlorobenzene is a resonance hybrid of the structures I to V. The mesomeric effect results in electronic displacement away from Cl (+M effect). In addition to +M effect the electromeric effect (+E) will be brought into play as under :



Thus for C_6H_5Cl we have +M, +E and —I effects, *i.e.*, +T and —I effects.

Thus electron attracting power (—I effect) of an atom alone cannot decide whether the substituent atom or group is o- and p-directing or m-directing.

For example, OH and NH_2 have a strong —I effect which tends to promote *m*-substitution. Since the mesomeric (+R) effect in their case is stronger than the —I effect, due to favourable overlap of 2 *p*-orbital of carbon and a 2 *p*-orbital of oxygen (see page 2·467), these groups become *o p*-orienting (with activation of the ring).

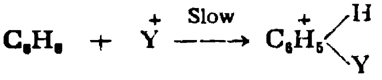
Chlorine atom in chlorobenzene has —I and +R effect and —I effect is greater than the +R effect. The —I effect deactivates the ring while the +R effect is too small to be significant. However, when the +E effect is brought into play at the requirement of the attacking reagent, the electron density at the *o*- and *p*-position becomes greater than that at the *m*-position though not so great as in benzene itself chlorine atom is, therefore, *o p*-directing with deactivation.

Some other compounds which give *o*-*p*-orientation with deactivation are styrene, benzyl chloride and cinnamic acid.

As stated earlier when an *o*-*p*-directing group as well as a *m*-directing group are present in the nucleus, directive influence of the *o*-*p*-directing group is stronger than that of the *m*-directing group. The above arguments can be extended to explain this.

(2) **Reactivity and Orientation based on carbocation (σ-complex) stability.**

Whatever the specific reagent used, the rate of the electrophilic aromatic substitution is determined by the same slow step—attack of the electrophile on the ring to form a carbocation :



$$C_6H_6 + \overset{+}{Y} \xrightarrow{\text{Slow}} \overset{+}{C_6H_5}\begin{smallmatrix}H\\Y\end{smallmatrix}$$

Rate-determining step

Electrophile Carbocation

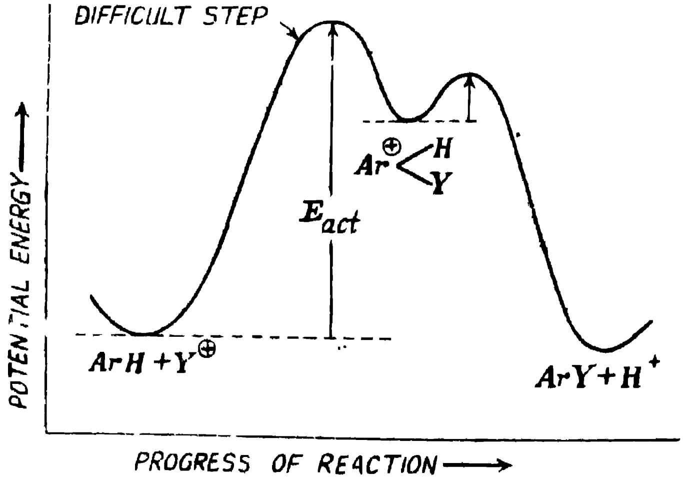
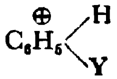


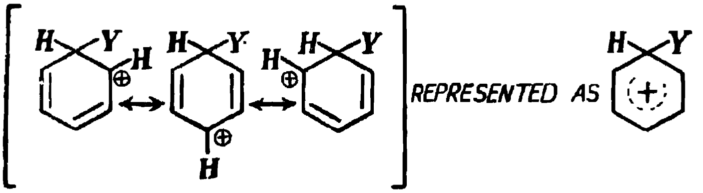
Fig. 34·2—Potential energy changes during the course of an electrophilic aromatic substitution reaction. Formation of carbocation is the rate-determining step.

Any differences in the rate of substitution must, therefore, be due to differences in the rate of this step.

For closely related reactions, a difference in the rate of formation of carbocation is determined by the difference in the needed energy of activation, E_{act}, *i.e.*, by a difference in the stability of the transition states. A dispersal of the positive charge stabilizes the incipient carbocation of the transition state. Further, we can expect a more stable carbocation to be formed more rapidly. Let us, therefore, concentrate on the relative stabilities of the carbocations.

The intermediate carbocation  $\overset{\oplus}{C_6H_5}\langle^{H}_{Y}$ is a resonance hybrid of structures I, II and III, in which the positive charge is distributed about the ring, being strongest at the positions ortho and para to the carbon atom being attacked.

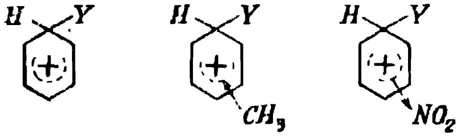
A group already present affects the stability of the carbocation by dispersing or intensifying the positive charge, depending upon



I II III

its electron-releasing or electron-withdrawing nature. This effect is specially important when the group is present in the ortho or para positions of the carbon being attacked.

Theory of Reactivity. In order to compare the rates of substitution in benzene, toluene and nitrobenzene, let us compare the following carbocations obtained from these.



I II III

In II, the methyl group releases electrons and tends to neutralize positive charge of the ring and becomes more positive itself. This dispersal of charge results in stabilization of the carbocation. In the same way, the inductive effect stabilizes the developing positive charge in the transition state and thus leading to a faster reaction.

In III, the nitro group on the other hand has an electron-withdrawing inductive effect which tends to intensify the positive charge and destabilize the carbocation, resulting in slower reaction.

Energy profiles for the formation of the σ complexes in the three cases given above are shown in Fig. 34·3.

As shown in Fig. 34·3 the energy of activation for an electrophilic attack on nitrobenzene, $E_{act\ (1)}$ is greater than the energy of activation for an electrophilic attack on benzene, $E_{act\ (2)}$. This

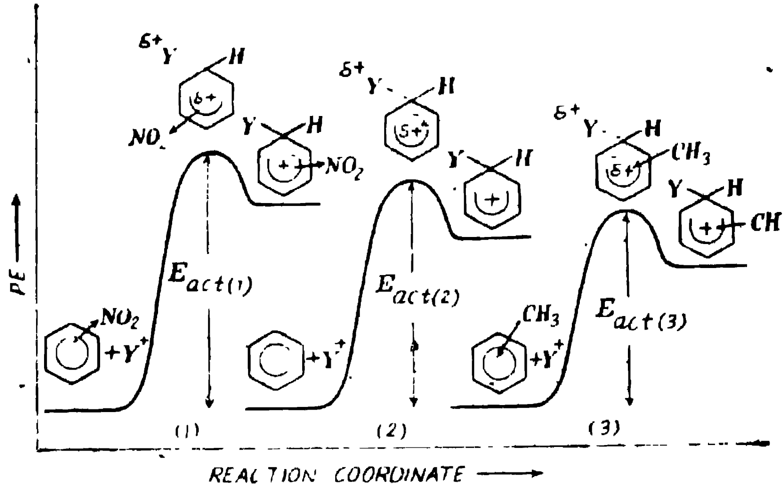


Fig. 34·3—Energy profiles for the formation of σ complex in electrophilic aromatic substitution reactions of (1) Nitrobenzene, (2) Benzene and (3) Toluene. In (1) NO_2 group is an electron-withdrawing group and in (3) CH_3 group is an electron-releasing group.

$$E_{act\ (1)} > E_{act\ (2)} > E_{act\ (3)}$$

has been explained in terms of the electron-withdrawing inductive effect of the nitro group. In fact $E_{act\ (1)}$ is substantially greater than $E_{act\ (2)}$ as a result of the combined effect of resonance and inductive effects as illustrated in Fig. 34·4.

P.E. of nitrobenzene is lower than that of benzene due to resonance.

P.E. of σ complex obtained from nitrobenzene is higher than that of σ complex obtained from benzene on account of inductive effect of the nitro group.

Theory of Orientation. An activating group activates all positions of the benzene ring. Its ortho and para-directing influence is due to the fact that it activates these positions much more as compared to the meta position.

A deactivating group deactivates all positions in the ring. Its meta directing influence is due to the fact that it deactivates the ortho and para positions to a greater degree than it does the meta position.

Thus we find that ortho, para orientation and meta orientation both arise in the same way ; *the activating or deactivating effect of any group is the strongest at the ortho-para positions.*

The observed facts are in accordance with theoretical reasoning based on the nature of carbocation obtained in each case. For example, the carbocation formed by attack at ortho, para and

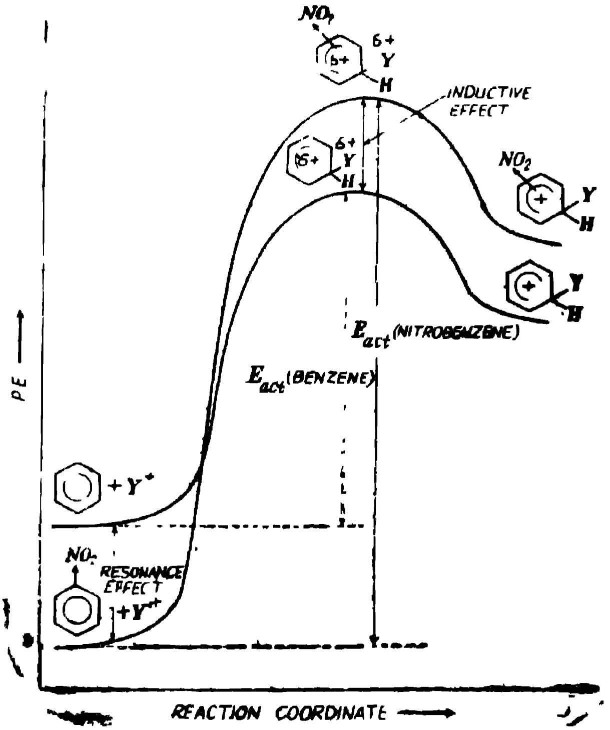
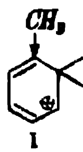
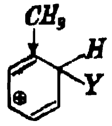


Fig. 34·4—Energy of activation for an electrophilic attack on nitrobenzene is substantially greater than that for an electrophilic attack on benzene due to the combined effect of resonance and inductive effects.

meta positions of toluene is in each case a hybrid of three structures as given below :



I



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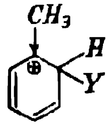
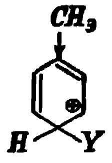


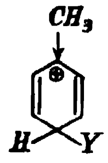
III

Especially stable : charge on carbon carrying substituent

ortho attack

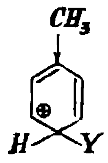


IV



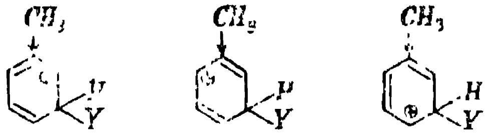
V

Especially stable : charge on carbon carrying substituent



VI

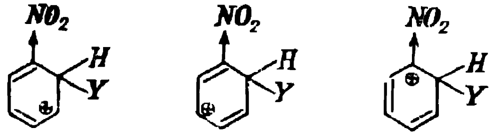
para attack



VII VIII IX *meta attack*

CH_3 is an activating group being electron-releasing. It releases electrons to all positions of the ring but does so most strongly to the carbon atom nearest to it. Consequently structures III (in ortho attack) and V (in para attack) are particularly stable. Ortho-para substitution in toluene is thus faster than meta substitution.

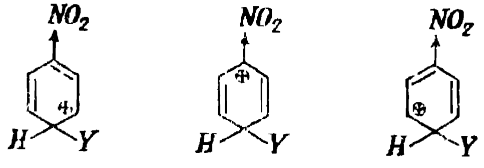
In nitrobenzene, the NO_2 group is electron-withdrawing and hence a deactivating group. The carbocation formed by attack at the ortho-para and meta positions is a hybrid of three structures given below in each case :



I II III *Ortho attack*

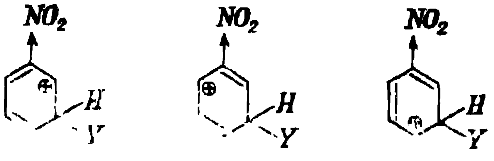
Especially unstable : charge on carbon carrying substituent

In two of the nine structures (III in ortho and V in para), the positive charge is located on the carbon atom to which NO_2 group is attached. Although $-NO_2$ group withdraws electrons from all positions, it does so most from the carbon atom nearest to it. This carbon atom, being already positive, has little



IV V VI *para attack*

Especially unstable : charge on carbon carrying substituent

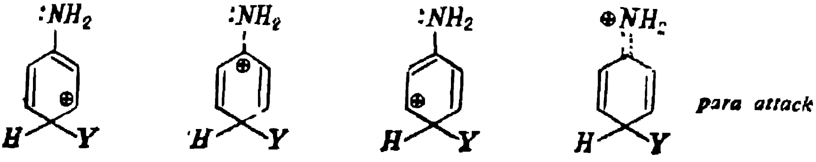


VII VIII IX *meta attack*

tendency to accommodate the positive charge of the carbocation. Structures III (in ortho attack) and V (in para attack) are thus especially unstable and do little to help stabilize the carbocation. The resulting cation is virtually a hybrid of only two structures (I & II in case of ortho attack and IV & VI in the case of para attack) ; and the positive charge is mainly restricted to only two carbon atoms. Carbocation resulting from meta attack being hybrid of three structures and in which positive charge is accommodated by three carbon atoms is more stable. In nitrobenzene, the ortho-para subtitution is thus slower than meta substitution.

Thus we find that ortho-para orientation by activating groups and meta orientation by deactivating groups both follow logically from the structure of carbocation. The charge of the carbocation is strongest at the positions ortho and para to the point of attack by an electrophile Hence a group (activating or deactivating) attached to these positions can exert the strongest effect.

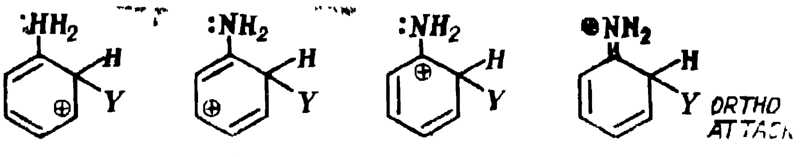
Electron Release by Resonance. So far we have considered electron-release or electron-withdrawal only as effects due to the electronegativity of the group concerned (*i.e., Inductive effect*). But groups like $—NH_2$, $—OH$, and their derivatives act as powerful activators towards electrophilic aromatic substitution even though they contain electronegative atoms which exert electron-withdrawing inductive effects. These groups release electrons by resonance effect. For example, the carbocation formed by attack at para position to NH_2 group in aniline is hybrid of structures I to IV, in which IV is especially stable since in this every atom has a complete octet of electrons except of course hydrogen which has a duplet.



I II III IV

Especially stable : every atom has an octet

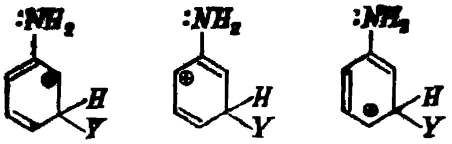
Corresponding structures for ortho attack (V to VIII) are such like I to IV. Among these structures VIII is especially stable for the same reason.



V VI VII VIII

Especially stable : every atom has an octet

These carbocations are much more stable than the one obtained by attack on benzene itself, or one obtained (IX to XI) from attack in meta position. In neither of these there is any especially stable structure like IV or VIII possible.

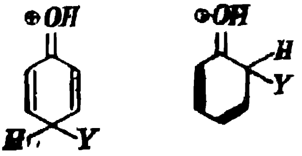


IX X XI

Meta attack

Thus substitution in aniline occurs faster than in benzene and occurs predominantly in the positions ortho and para to the —NH_2 group.

Similarly, activation by the —OH group and its ortho-para orientation is due to contribution of structures given below in which *every atom has a complete octet of electrons.*



para attack *ortho attack*

Summary. Thus we see that both reactivity and orientation in electrophilic aromatic substitution are determined by the rates of formation of the intermediate carbocations. These rates depend upon the stabilities of those carbocations which are determined by the electron-releasing or electron-withdrawing properties of the substituent groups already present.

The halo groups are the only ortho-para directors that are also deactivating. We can account for this peculiar behaviour of the halo groups on the assumption that their inductive effect governs reactivity whereas their resonance coupled with electromeric effect influences orientation (*see* page 2·460).

Through their electron-withdrawing inductive effect the halo groups make the ring slightly positively charged. As a result of it energy of activation for an electrophilic aromatic substitution for halobenzene is greater than that for benzene. In other words, a halo group deactivates the benzene ring.

On the other hand when an electrophilic attack does take place, the halo group stabilises the σ-complexes resulting from ortho and para attack by resonance by donating a pair of non-bonding electrons. This makes halo substituents ortho-para directors.

However, we come across an apparent contradiction. Oxygen is more electronegative than chlorine or bromine. Yet, the OH group is an activating group while Cl or Br are deactivating. This is explained in terms of the relative stabilisation caused by electron donation in each case.

Resonance structure resulting from electron donation by $\ddot{O}H$ or $\ddot{N}H_2$ involves a favourable overlap of $2p$ orbital of carbon and a $2p$ orbital of oxygen or nitrogen. Overlap is favourable since the atoms are almost of the same size. With chlorine the electron donation involves an overlap of $2p$ orbital of carbon with a $3p$ orbital of chlorine. This overlap is less effective as chlorine atom is much longer and its $3p$ orbital is much farther from its nucleus. With bromine or iodine the overlap is even less effective.

Carbon and fluorine atoms being almost of the same size, the overlap of $2p$ orbital of carbon and $2p$ orbital of fluorine is very effective and hence favourable. Fluorobenzene is, therefore, most reactive halobenzene in spite of its high electronegativity.

TEST YOUR UNDERSTANDING

1. Fill in the blanks in the following :

(*i*) Aromatic hydrocarbons have a tendency to undergo.......substitution

(*ii*) Aliphatic hydrocarbons undergo chiefly addition at multiple bonds and . .. substitution at other points along the chain.

(*iii*) As the size of the entering group increases, the amount of ortho isomer obtained......

(*iv*) A positive charge on XY makes it......directing.

(*v*) In electrophilic substitution, a group already present increases the stability of the carbocation by.........the positive charge depending upon its electron...... nature.

✓(*vi*) A carbocation is especially stable if the charge is on the carbon...... or if every atom has..octet

2. Give structures and names of the principal organic products expected from mononitration of :

(*a*) *o*-nitrotoluene,

(*b*) *p*-nitroacetanilide,

(*c*) *o*-cresol,

(*d*) *m*-nitrotoluene,

(*e*) *m*-dibromobenzene,

(*f*) *p*-cresol,

(*g*) aniline hydrogen sulphate.

3. Arrange the following in order of reactivity towards electrophilic substitution listing the most reactive structure at the bottom :

(*i*) Benzene, bromobenzene, nitrobenzene, toluene.

(*ii*) Acetanilide, acetophenone, aniline, benzene.

(*iii*) Chlorobenzene, *p*-chloronitrobenzene, 2, 4-dinitrochlorobenzene

(*iv*) Phenol, aniline, toluene, nitrobenzene.

4. 1, 3, 5-trinitrobenzene (TNB) has more shattering power than 2, 4, 6-trinitrotoluene (TNT), and it is no more dangerous to handle. Can you suggest a reason (connected with its manufacture) why TNT is still in more general use as high explosive ? (Benzene and toluene are both readily available and benzene is rather cheaper).

KEY

1. (*i*) ionic ; (*ii*) free radical ; (*iii*) decreases ;
(*iv*) meta ; (*v*) dispersing, releasing :
(*vi*) carrying an electron-releasing substituent, an octet.

3. Consult Table 34·1.

QUESTIONS

Essay Type :

1. What do you understand by the term Orientation ? Explain with the aid of examples how this has been carried out in the case of di- and trisubstitution products of benzene.

2. There are three dibromobenzenes, melting at 360K, 279K and 266K. Identify them with the help of the following results :

(*a*) The one melting at 360K yields one mononitro derivative on nitration.

(*b*) The second (m.p. 279K) yields two mononitro derivatives.

(*c*) The third (m.p. 266 K) yields three mononitro derivatives.

3. How many trimethylbenzenes are there ? How many mononitro derivatives will be given by each one of these ?

4. Six diaminobenzoic acids are known. Each one of these on decarboxylation yields one or more diaminobenzenes as follows :

(*i*) Three of these acids produced a single diaminobenzene (m.p. 336 K).

(*ii*) Two of these gave another diaminobenzene (m.p. 377K).

(*iii*) One of these gave diaminobenzene (m.p. 415 K).

With the help of the above data, answer the following questions :

(*a*) What are the structures of three diaminobenzenes melting at 336K, 377K and 415K respectively ?

(*b*) What are the structures of the six diaminobenzoic acids which yield these diaminobenzenes on decarboxylation ?

5. Where a mono-substituted benzene compound is converted into disubstituted compound, explain with examples how the group already present in the ring exerts a directing influence on the entering group.

6. Write an essay on the directive influence of substituents on further substitution in the benzene ring. Show what compounds are formed when (*a*) toluene, (*b*) phenol, (*c*) benzaldehyde, (*d*) benzoic acid, (*e*) *m*-xylene, (*f*) *p*-aminophenol, and (*g*) *p*-cresol are nitrated.

7. Discuss the general laws of substitution. What products will predominate in the following reactions :

(*a*) Nitration of acetophenone or chlorobenzene.
(*b*) Bromination of nitrobenzene, aniline or phenol.
(*c*) Chlorination of phenol, aniline or bromobenzene.
(*d*) Sulphonation of benzaldehyde, benzoic acid, or toluene.
(*e*) Nitration of benzonitrile, benzenesulphonic acid or benzoic acid : *(Delhi B.Sc. 1974)*

8. Write a note on the characteristics of aromatic compounds.

9. Write an account of the mechanism of aromatic substitution with reference to electrophilic, nucleophilic and free radical mechanisms.

10. Giving two suitable examples, illustrate directive influence in aromatic compounds. *(Delhi B.Sc. Hons. 1980)*

11. How do you investigate whether a certain group is an activating group or a deactivating one ? State the rule governing orientation in terms of electron-releasing and electron-withdrawing groups.

12. Write an essay on Reactivity and Orientation.

13. Write short notes on :

(*i*) Theory of Orientation.

(*ii*) Theory of Reactivity.

14. Write a short essay on : 'Electron release by Resonance'.

Short Answer Type :

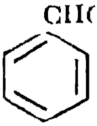
1. What are the functional groups and the general formulae of the following homologous series :

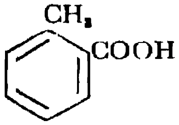
Aromatic hydrocarbons
Aromatic amines
Aromatic alcohols
Aromatic acids
Aromatic aldehydes
Diazo compounds
Sulphonic acids
Nitro compounds
Amino compounds

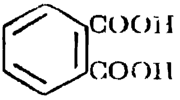
2. Write formulae for the following organic compounds, giving graphic formulae, wherever necessary :

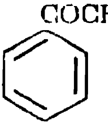
o- xylene
Benzyl chloride
o-toluidine
Benzylamine
o-Benzenedisulphonic acid
Trinitrotoluene
Benzyl alcohol
Phthalic acid
m- Toluic acid
1, 2, 4-Benzenetriol
m-dichlorobenzene
Benzenesulphonic acid
Benzylidene chloride
p-dinitrobenzene
Benzenediazonium chloride
Salicylaldehyde
1, 3-Benzenediol
Ethoxybenzene
Benzaldehyde
Benzophenone
Benzal chloride
Dimethylaniline
Phenyl chloride
Triphenylamine
3-Methylphenol
1, 2-Benzenediol
1, 2, 3-Benzenetriol
Acetophenone
Salicylic acid
m-Chlorotoluene
p-Toluidine

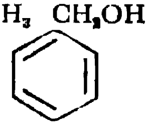
3. Write names of the compounds whose formulae are given below :

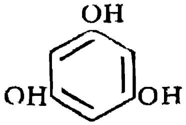


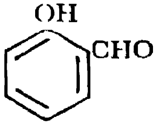


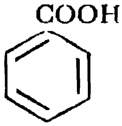


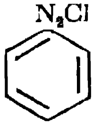


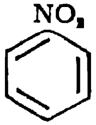


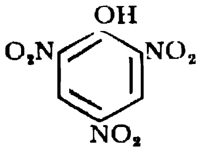


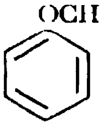


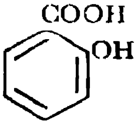


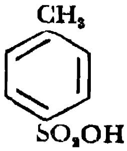


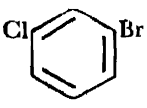


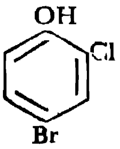


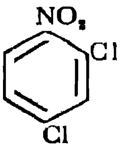


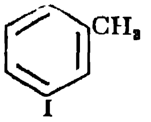


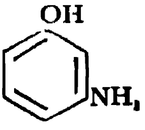


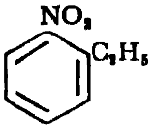


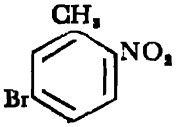


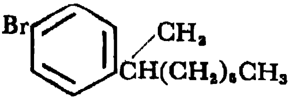


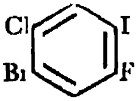


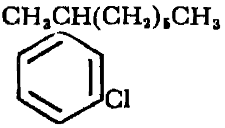






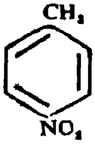


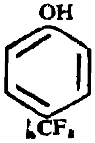


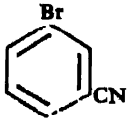


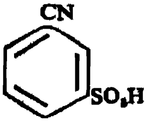
4. Write structural formulae and give names for various isomers of the following : (*a*) Tribromobenzenes, (*b*) Dichloronitrobenzenes, (*c*) Dinitrotoluenes, and (*d*) Methylphenols.

5. Predict the major product (or products) which would be obtained on mononitration of each of the following compounds:

(a)


(b)


(c)


(d)


6. State reasons for the following facts :

(a) $-\ddot{N}H_2$, $-\ddot{O}CH_3$, $-\ddot{N}H.COCH_3$ and $-Cl$ are ortho-para orienting groups.

(b) $-CO_2H$, $-NO_2$ are *m*-directing groups.

7. Write mechanism for electrophilic substitution in a benzene ring by giving the essential steps involved.

8. What do you understand by

(i) Mesomeric effect ; (ii) Electromeric effect ;
(iii) Inductive effect (iv) Conjugative effect.

9. Out of the conjugative effect and inductive effect which is more powerful ?

10. Discuss the mechanism of nucleophilic substitution in benzene ring.

11. Give one example of an S_N1 reaction.

12. Give one example of an S_N2 reaction.

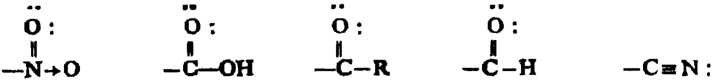
13. Electron-releasing groups are ortho- and para-directors whereas electron-withdrawing groups are meta-directors.

Give two examples each of these two types of groups. Which of these are activating groups and which are deactivating groups ?

14. Discuss the activating effect of a $-NO_2$ group present in *o*-chloronitrobenzene.

15. Give a brief account of the theory of reactivity.

16. Nitrobenzene stabilises itself by resonance as shown on page 2·455. The following groups are of the same type :



$$\overset{\ddot{O}:}{\overset{\|}{-N}}\rightarrow O \qquad \overset{\ddot{O}:}{\overset{\|}{-C}}-OH \qquad \overset{\ddot{O}:}{\overset{\|}{-C}}-R \qquad \overset{\ddot{O}:}{\overset{\|}{-C}}-H \qquad -C\equiv N:$$

Write resonance structures showing stabilization by resonance of the benzene compounds containing each of these groups.

17. (a) Write one resonance structure for acetanilide which does not involve electrons of the ring. You will find it involves (+) and (−) charges.

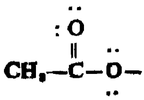
(b) Explain on the basis of the resonance structure written by you, why acetanilide is less reactive towards electrophilic substitution than aniline.

(c) Acetamido group ($-NHCOCH_3$) is an ortho-para director and acetanilide is much more reactive than benzene.

Can you account for these facts on the basis of resonance structures which involve the benzene ring ?

(d) Do you expect phenyl acetate to be more or less reactive than phenol. Give reasons.

(e) What is the directive influence of acetoxy group,



$$CH_3-\overset{\overset{\ddot{}}{:O}}{\overset{\|}{C}}-\ddot{\underset{\cdot\cdot}{O}}-$$

in phenyl acetate ?

(*f*) Compared to benzene, is phenyl acetate more or less reactive in electrophilic substitution ?

18. Why does nitration of nitrobenzene give *m*-dinitrobenzene while nitration of chlorobenzene gives *o*- and *p*-nitrochlorobenzene ? 5
(*Delhi B.Sc. Hons. 1980*)

19. Explain why bromination of nitrobenzene is difficult but nitration of bromobenzene is easy. (*Delhi B.Sc. 1980*)

20. (*a*) Explain why the bromination of aniline gives 2, 4, 6-tribromoaniline whereas nitration of aniline with mixed acid gives *m*-nitroaniline.

(*b*) Toluene is *o*-*p*-directing whereas trichloromethylbenzene is *m*-directing, Explain.

(*c*) Would you expect *p*-nitrochlorobenzene to be more or less reactive than chlorobenzene towards hydroxide ion ? Explain.
(*Delhi B.Sc. Hons. 1979*)

21. (*a*) Explain why, in electrophilic substitution reactions—

(*i*) aniline reacts faster than nitrobenzene.

(*ii*) the directive influence of amino and nitro groups are different.

(*b*) Compare the relative ease of nucleophilic substitution in chlorobenzene, *p*-nitrochlorobenzene and benzyl chloride.

(*a*) Where will further substitution (*e.g.*, mononitration) occur in the following :

(*i*) *N*-acetyl derivative of *p*-toluidine, and (*ii*) *m*-bromobenzoic acid.
(*Delhi B.Sc. Hons. 1979*)

22. What is the difference between a transition state and an intermediate in an organic reaction ? Briefly describe. (*Kerala B.Sc. 1981*)

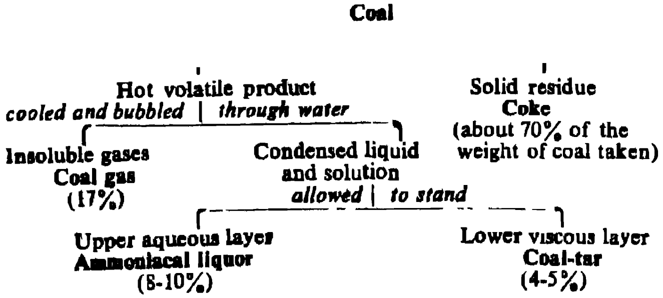
23. Classify the following into +I and —I groups :
Isopropyl, cyano, methoxy and *tert*-butyl. (*Kerala B.Sc. 1981*)

35

Coal-tar

1. Destructive Distillation of Coal.—Coal is not merely free carbon as we commonly believe, it is a mixture of a number of complex organic compounds. For example, bituminous coal contains about 32-40 per cent of volatile matter (*organic compounds*).

When bituminous coal is subjected to destructive distillation at 1270-1670K, it yields the following chief products :



Coal is also distilled at low temperatures (about 870K) for the production of smokeless fuel such as "coalite". The yield of coal gas and tar is doubled. Coal-tar obtained is rich in aliphatic compounds.

Coal gas obtained in high temperature distillation contains some benzene and toluene vapours which contribute greatly to its illuminating power. These hydrocarbons may be extracted from coal gas by scrubbing it with creosote oil (*see* § 3). Creosote oil dissolves these vapours and gives them back on distillation in the form of *light oil*. At most of the gas works, however, these are allowed to remain in the gas. Coal gas is usually burnt as fuel and not used as a source of chemical substances.

One tonne of coal on destructive distillation yields approximately the following products :

Coke	...700 kg.	Ammonium sulphate	...12 kg.
Coal gas	...311,000 litres	Light oil	.. 18 litres
Coal-tar	...40-60 litres		

In India large quantities of coal are being mined at Jharia, Raniganj, Bokaro, Giridih, Karanpura and some of it in Assam. Coal gas is unknown in this country except in a few cities where it is used for illumination. Here we are carrying on destructive distillation of coal for the manufacture of coke used in iron industries. One of the world's largest coking plants is working at Jamshedpur and is owned by Tate Iron and Steel Co. Ltd.

2. **Coal-tar.**—It is a black viscous liquid with unpleasant smell, obtained as by-product during the manufacture of coal gas by destructive distillation of coal. Actual composition of coal-tar varies with the nature of coal and carbonising temperature. In addition to the carbon particles, to which it owes its black colour, the common substances present in coal-tar are :

Neutral :	Hydrocarbons—Benzene, Toluene, Naphthalene, Anthracene, etc.
Acidic :	Phenol (carbolic acid), Cresol, etc.
Basic :	Pyridine, etc.

At one time coal-tar was not only a waste product but also a veritable nuisance. People thanked their stars when it was found that coal-tar could be used for the metalling of roads. Modern researches have shown it to be a valuable treasure which supplies us the starting material for a large number of products used in everyday life and industry, *e.g.*, synthetic dyes, drugs, explosives, perfumes and photo goods.

3. **Fractional Distillation of Coal-tar.**—Different compounds present in coal-tar are separated by fractional distillation as follows :

Coal-tar is taken in a pre-heater where it is heated by a pipe through which are passing hot vapours from the still. Here it loses most of the water present (which would otherwise give violent frothing) along with some low-boiling hydrocarbons. From the pre-heater it flows into an iron still heated in a furnace. Different fractions distil over at different temperatures and are collected separately.

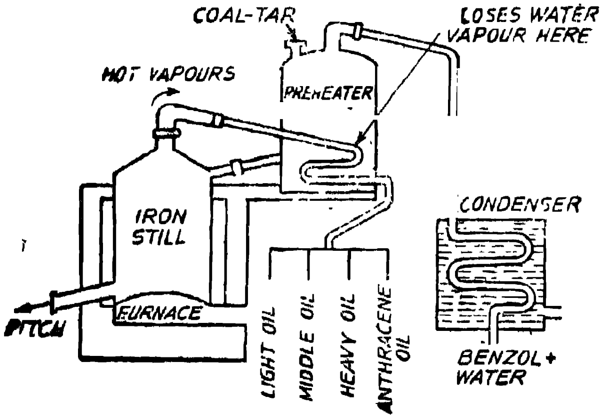
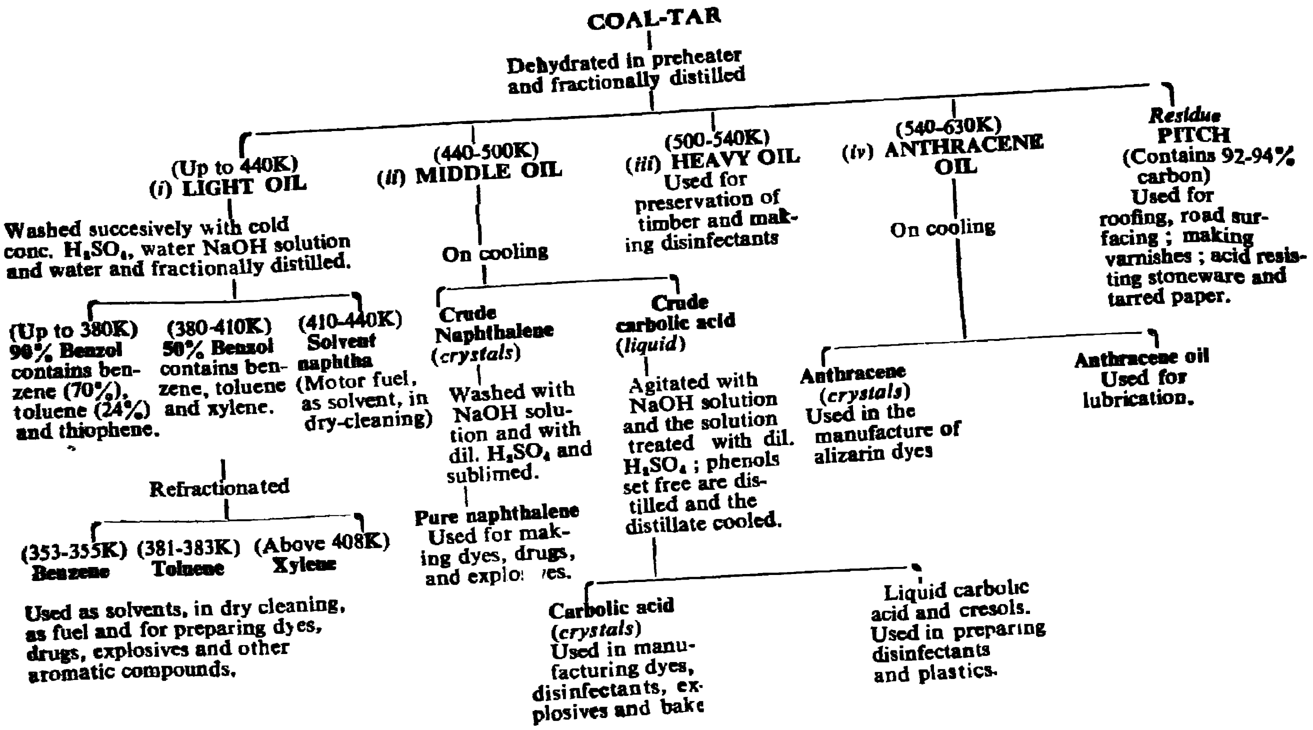


Fig. 35·1—Fractional distillation of coal-tar.

Different Products and Their Uses. Various fractions obtained and the uses to which they are put, are given below :

(1) **Light Oil or Crude Naphtha** (*up to 440K*) is the first fraction and is named so being lighter than water. It is treated with cold concentrated sulphuric acid to remove basic substances, *e.g.*, pyridine, and then washed with water and treated with caustic soda,


COAL-TAR
Dehydrated in preheater and fractionally distilled
(Up to 440K) (i) LIGHT OIL
Washed succesively with cold conc. H_2SO_4, water NaOH solution and water and fractionally distilled.
(Up to 380K) 90% Benzol contains benzene (70%), toluene (24%) and thiophene.
(380-410K) 50% Benzol contains benzene, toluene and xylene.
(410-440K) Solvent naphtha (Motor fuel, as solvent, in dry-cleaning)
Refractionated
(353-355K) Benzene
(381-383K) Toluene
(Above 408K) Xylene
Used as solvents, in dry cleaning, as fuel and for preparing dyes, drugs, explosives and other aromatic compounds.
(440-500K) (ii) MIDDLE OIL
On cooling
Crude Naphthalene (crystals)
Washed with NaOH solution and with dil. H_2SO_4 and sublimed.
Pure naphthalene Used for making dyes, drugs, and explo: /es.
Crude carbolic acid (liquid)
Agitated with NaOH solution and the solution treated with dil. H_2SO_4; phenols set free are distilled and the distillate cooled.
Carbolic acid (crystals) Used in manufacturing dyes, disinfectants, explosives and bake
Liquid carbolic acid and cresols. Used in preparing disinfectants and plastics.
(500-540K) (iii) HEAVY OIL Used for preservation of timber and making disinfectants
(540-630K) (iv) ANTHRACENE OIL
On cooling
Anthracene (crystals) Used in the manufacture of alizarin dyes
Anthracene oil Used for lubrication.
Residue PITCH (Contains 92-94% carbon) Used for roofing, road surfacing; making varnishes; acid resisting stoneware and tarred paper.

to remove acidic substances, *e.g.*, phenol and excess sulphuric acid. It is then washed with water and subjected to fractional distillation when we get :

(*a*) *90% Benzol* (350-380K) containing *benzene and toluene.* Actually it contains 70% of benzene. It is called "90% benzol" because 100 cm^3 of the fraction, when distilled, yield 90 cm^3 of distillate below 373K.

(*b*) *50% Benzol* (380-410K) containing the same two hydrocarbons in different proportions along with *xylene.* It contains 46% of benzene.

(*c*) *Solvent Naphtha or Benzine* (410-440K) containing *xylene, mesitylene, etc.*

The various hydrocarbons obtained are used as solvent in dry-cleaning, as fuel and as starting materials for the manufacture of various explosives, dyes, drugs and perfumes.

(2) **Middle oil or Carbolic oil** (440-500K). Middle oil contains mainly naphthalene and carbolic acid (phenol). On allowing it to stand naphthalene crystallizes out and is separated in a centrifugal machine. The residue is treated with caustic soda and the aqueous solution is separated and treated with dilute sulphuric acid to regenerate carbolic acid used in the preparation of disinfectants, bakelite, plastics and explosives. Naphthalene obtained is washed with sodium hydroxide and then with sulphuric acid. It is next purified by sublimation and used for the manufacture of explosives, dyes and insecticides.

(3) **Heavy oil or Creosote oil** (500-540K). It is greenish yellow oil, heavier than water. It contains mainly cresols and is used as such for preservation of wood and the manufacture of disinfectants.

(4) **Anthracene oil or Green oil** (540-630K). Anthracene oil contains anthracene and phenanthrene which are deposited as crystals on cooling. These find use in the manufacture of alizarin dyes. The oil shows green fluorescence and is, therefore, called '*green oil*'.

(5) **Pitch** (92-94% *Carbon*). The black residue, left in the still after the distillation is over, is called *pitch.* It contains 92-94 per cent of carbon and finds use in varnishes, road-making and protecting wood and metal work. It is also used as a binder in making coal-briquettes used as fuel.

QUESTIONS

Essay Type :

1. Describe coal-tar distillation. Give important uses of various products obtained.

2. How is pure benzene isolated from coal-tar ? (*Marathwada B.Sc. 1976*)

Short Answer Type :

1. Name various fractions of coal-tar distillation giving temperatures at which these distil over.
2. What is contained in middle oil fraction ?
3. What are major constituents of the light oil fraction ?
4. What are the main constituents of heavy oil and green oil ?
5. What is pitch ? What is it used for ?

36

Benzene and Its Homologues (Arenes)

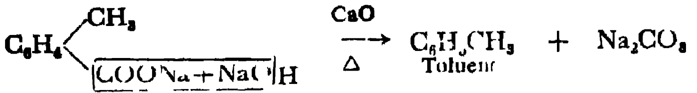
1. Aromatic Hydrocarbons.—The general formula of the homologous series is C_nH_{2n-6}. Benzene, C_6H_6 is the first member of the homologous series. Its higher homologues are toluene ($C_6H_5CH_3$) and xylene, $C_6H_4(CH_3)_2$. Xylene shows position isomerism and three isomeric xylenes ortho-, meta-, and para- are known. Coal-tar constitutes the chief source of these hydrocarbons although small amounts also occur in natural petroleum.

2. General Methods of Preparation of Benzene and its Homologues :

(*a*) **Methods involving removal of the group already present in the nucleus :**

(*i*) *By heating an aromatic acid or its sodium salt with soda-lime (Removal of —COOH group)*

$$\underset{\text{Sod benzoate}}{C_6H_5\boxed{COONa + NaO}H} \xrightarrow[\Delta]{CaO} C_6H_6 + Na_2CO_3$$

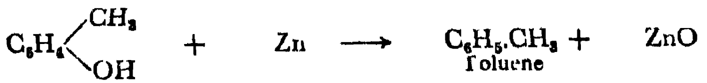


$$C_6H_4\begin{cases} CH_3 \\ \boxed{COONa + NaO}H \end{cases} \xrightarrow[\Delta]{CaO} \underset{\text{Toluene}}{C_6H_5CH_3} + Na_2CO_3$$

Sodium toluate

(*ii*) *By passing vapours of phenol over heated zinc dust (Removal of —OH group).*

$$\underset{\text{Phenol}}{C_6H_5OH} + Zn \longrightarrow \underset{\text{Benzene}}{C_6H_6} + ZnO$$

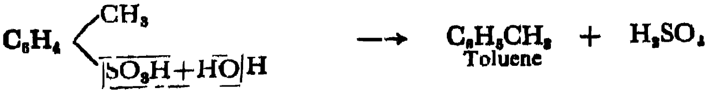


$$C_6H_4\begin{cases} CH_3 \\ OH \end{cases} + Zn \longrightarrow \underset{\text{Toluene}}{C_6H_5.CH_3} + ZnO$$

o-, *m*-, or *p*-methylphenol

(*iii*) *By the hydrolysis of sulphonic acids with superheated steam or by boiling with dilute hydrochloric acid under pressure at 420-470K (Removal of —SO_3H).*

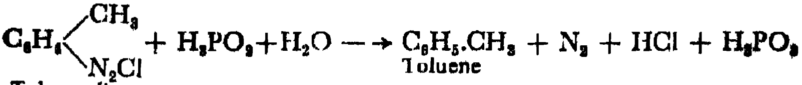
$$\underset{\text{Benzenesulphonic acid}}{C_6H_5\boxed{SO_3H + HO}H} \longrightarrow \underset{\text{Benzene}}{C_6H_6} + H_2SO_4$$



$$C_6H_4\begin{cases} CH_3 \\ \boxed{SO_3H + HO}H \end{cases} \longrightarrow \underset{\text{Toluene}}{C_6H_5CH_3} + H_2SO_4$$

o-, *m*-, & *p*- Toluene-Sulphonic acid *(iv) By the action of hypophosphorous acid, H_3PO_2 (reducing agent) on arenediazonium salts (Removal of —N=N.Cl group).*

$$\underset{\text{Benzenediazonium chloride}}{C_6H_5N_2Cl} + H_3PO_2 + H_2O \longrightarrow \underset{\text{Benzene}}{C_6H_6} + N_2 + HCl + H_3PO_3$$



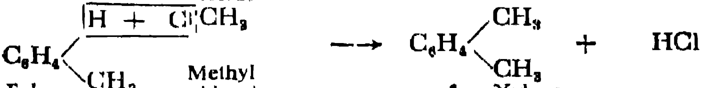
$$C_6H_4\begin{cases}CH_3\\N_2Cl\end{cases} + H_3PO_2 + H_2O \dashrightarrow \underset{\text{Toluene}}{C_6H_5.CH_3} + N_2 + HCl + H_3PO_3$$

Toluenediazonium chloride

(b) Methods involving addition of one or more alkyl groups to the benzene nucleus :

(v) By the action of alkyl halides on benzene in presence of anhydrous aluminium chloride— catalyst (**Friedel-Crafts reaction**).

$$\underset{\text{Benzene}}{C_6H_5|\overline{H}} + \underset{\text{Methyl chloride}}{\overline{Cl}|CH_3} \xrightarrow{AlCl_3} \underset{\text{Toluene}}{C_6H_5.CH_3} + HCl$$

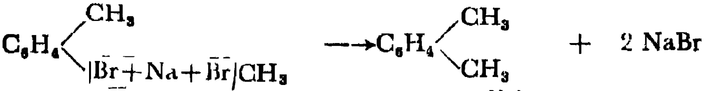


$$\underset{\text{Toluene}}{C_6H_4\begin{cases}H\\CH_3\end{cases}} + \underset{\text{Methyl chloride}}{Cl|CH_3} \longrightarrow \underset{\text{o- \& p- Xylene}}{C_6H_4\begin{cases}CH_3\\CH_3\end{cases}} + HCl$$

For mechanism see page 2·485.

(vi) By heating halogen derivative of benzene or one of its homologues and an alkyl halide with metallic sodium in dry ether (**Wurtz-Fittig reaction**).

$$\underset{\text{Phenyl bromide}}{C_6H_5|Br} + 2Na + \underset{\text{Methyl iodide}}{I|CH_3} \longrightarrow \underset{\text{Toluene}}{C_6H_5.CH_3} + NaBr + NaI \ (60\%)$$



$$\underset{\text{o-, m-, or p-bromotoluene}}{C_6H_4\begin{cases}CH_3\\Br\end{cases}} + Na + \underset{\text{Methyl bromide}}{Br|CH_3} \longrightarrow \underset{\text{o-, m-, or p-Xylene}}{C_6H_4\begin{cases}CH_3\\CH_3\end{cases}} + 2\,NaBr$$

Mechanism of Wurtz-Fittig Reaction. The mechanism of the Wurtz Fittin g reaction is uncertain. The following two mechanisms have been suggested:

(a) *Via the formation of organo-metallic compounds* :

(i) $C_6H_5Br + 2Na \longrightarrow C_6\overset{-}{H}_5\overset{+}{Na} + NaBr$

(ii) $C_6\overset{-}{H}_5\overset{+}{Na} + C_2H_5Br \longrightarrow C_6H_5.C_2H_5 + NaBr$

(iii) $C_2H_5Br + 2Na \longrightarrow C_2\overset{-}{H}_5\overset{+}{Na} + NaBr$

(iv) $C_6H_5Br + C_2\overset{-}{H}_5\overset{+}{Na} \longrightarrow C_6H_5.C_2H_5 + NaBr$

(v) $C_2H_5Br + C_6\overset{-}{H}_5\overset{+}{Na} \longrightarrow C_2H_5.C_6H_5 + NaBr$

Reaction (*i*) proceeds very much faster than (*ii*), the main reaction, therefore, is (*ii*) producing $C_6H_5.C_2H_5$.

Rudolph Fittig (1835-1910)—German chemist. Noted for synthetic work in the aromatic series ; the discoverer of phenanthrene in coal-tar.

(*b*) *Via the formation of free radicals* :

$$C_6H_5Br + Na \longrightarrow C_6H_5. + NaBr$$
$$2C_6H_5. \longrightarrow C_6H_5-C_6H_5 \ (Diphenyl)$$
$$C_2H_5Br + Na \longrightarrow C_2H_5. + NaBr$$
$$2C_2H_5. \longrightarrow C_2H_5-C_2H_5 \ (Butane)$$
$$C_6H_5. + C_2H_5. \longrightarrow C_6H_5-C_2H_5$$

$C_6H_5C_2H_5$ is the main product while diphenyl and butane are by-products.

(*vii*) *By treating a Grignard reagent* (*Arylmagnesium halide*) *with alkyl halide* (**Grignard reaction**) *in dry ether.*

$$\underset{\text{Phenylmagnesium bromide}}{C_6H_5|\overline{MgBr}} + \underset{\text{Methyl bromide}}{\underline{Br}|CH_3} \longrightarrow \underset{\text{Toluene}}{C_6H_5.CH_3} + MgBr_2 \quad (v.g.)$$

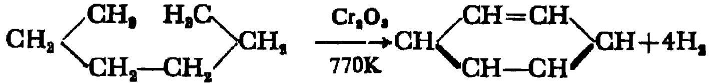
Other Methods :

(*viii*) *By Clemmensen reduction of ketones with zinc amalgam and hydrochloric acid.*

$$\underset{\text{Acetophenone}}{C_6H_5COCH_3 + 4[H]} \xrightarrow[+HCl]{Zn/Hg} \underset{\text{Ethylbenzene}}{C_6H_5CH_2CH_3} + H_2O$$

The ketone needed above may be prepared from benzene by Friedel-Crafts reaction.

(*ix*) *By cyclization of long-chain alkanes obtained from petroleum* Vapours of alkanes under pressure are passed over a chromium catalyst (Cr_2O_3 supported on Alumina) heated to 775K.



n-Hexane Benzene

In a similar way toluene is prepared from *n*-heptane and xylenes from *n*-octane.

$$\underset{n\text{-Heptane}}{CH_3.(CH_2)_5.CH_3} \longrightarrow \underset{\text{Toluene}}{C_6H_5.CH_3} + 4H_2$$

$$\underset{n\text{-Octane}}{CH_3.(CH_2)_6.CH_3} \xrightarrow{-4H_2} \underset{\text{Xylene}}{C_6H_4(CH_3)_2} + \underset{\text{Ethylbenzene}}{C_6H_5.C_2H_5}$$

Petroleum is proving to be an almost inexhaustible source of aromatic hydrocarbons which are formed there by cyclization of aliphatic hydrocarbons.

3. General Properties of Benzene and its Homologues.

Physical. Benzene and its homologues are usually colourless, refractive liquids, insoluble in water, but miscible with organic solvents in all proportions. Their vapours are inflammable, have a characteristic odour and are toxic in nature. The boiling points increase gradually with the rise of molecular weight.

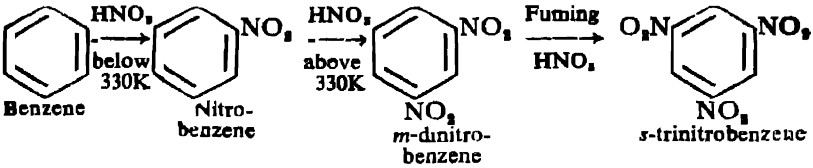
Hydrocarbon	*b. p.* (*K*)	*Hydrocarbon*	*b p.* (*K*)
Benzene, C_6H_6	353	*o*-Xylene, $C_6H_4(CH_3)_2$	417
Toluene, $C_6H_5.CH_3$	373	*m*- ,, ,, ,,	412
Ethylbenzene, $C_6H_5C_2H_5$	409	*p*- ,, ,, ,,	411
Propylbenzene, $C_6H_5C_3H_7$	432	Mesitylene, $C_6H_3(CH_3)_3$	538

Chemical. Benzene nucleus is unusually stable but the hydrogen atoms attached to the nucleus are readily replaced by other atoms or groups (*substitution reaction*). The side-chains are aliphatic in character. Their general reactions are :

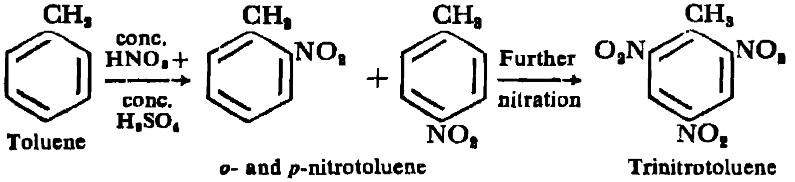
(1) **Combustion.** Benzene and its homologues are inflammable liquids and burn with a sooty flame giving carbon dioxide and water vapour.

$$2C_6H_6+15O_2 \longrightarrow 12CO_2 + 6H_2O$$
$$C_6H_5.CH_3+9O_2 \longrightarrow 7\,CO_2 + 4H_2O$$

(2) **Nitration.** When treated with a mixture of concentrated nitric acid and concentrated sulphuric acid below 330K, benzene gives nitrobenzene while above this temperature *m*-dinitrobenzene is the main product. With hot fuming nitric acid, and concentrated sulphuric acid, a third nitro group enters to give symmetrical trinitrobenzene.



Toluene can be nitrated more easily than benzene, main product of nitration being *o*- and *p*-nitrotoluene. Further nitration in presence of fuming nitric acid gives trinitrotoluene.



Mechanism of Nitration. The commonly accepted mechanism of nitration with a mixture of nitric and sulphuric acids involves the following sequence of reactions :

(*i*) $HONO_2 + 2H_2SO_4 \rightarrow H_3\overset{\oplus}{O}+2H\overset{\ominus}{SO_4} + \overset{\oplus}{NO_2}$

Nitronium ion

(*ii*) $\overset{\oplus}{NO_2} + C_6H_6 \rightarrow \overset{\oplus}{C_6H_6}\!<^{H}_{NO_2}$ (*slow*)

(*iii*) $\overset{\oplus}{C_6H_6}\!<^{H}_{NO_2} + HSO_4^- \rightarrow C_6H_5NO_2 + H_2SO_4$ (*fast*)

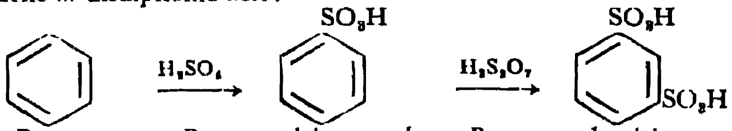
Step (*i*) generates the nitronium ion, $^+NO_2$ which is the electrophile that actually attacks the benzene ring. Strong sulphuric acid protonates nitric acid and causes it to split into $\overset{\oplus}{NO_2}$ and H_2O. Water is absorbed by H_2SO_4 to form $H_3\overset{\oplus}{O}$ and $H\overset{\ominus}{SO_4}$.

$$HO-NO_2 + H_2SO_4 \rightarrow \underset{H}{\overset{\oplus}{HO}}-NO_2 + \overset{\ominus}{HSO_4}$$

$$\underset{H}{\overset{\oplus}{HO}}-NO_2 \rightarrow H_2O + \overset{\oplus}{NO_2}$$

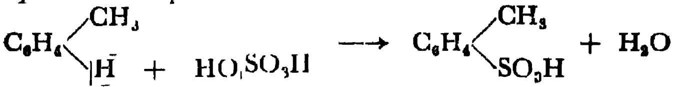
$$H_2O + H_2SO_4 \rightarrow \overset{\oplus}{H_3O} + \overset{\ominus}{HSO_4}$$

(3) **Sulphonation.** With hot concentrated sulphuric acid benzene gives benzenesulphonic acid while with oleum it yields benzene-*m*-disulphonic acid.



Benzene Benzene sulphonic acids Benzene-*m*-di-sulphonic acid

With concentrated sulphuric acid toluene gives a mixture of *o*- and *p*- toluenesulphonic acid.

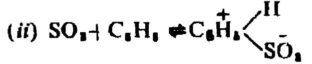


$$C_6H_4\langle^{CH_3}_{H} + HO.SO_3H \longrightarrow C_6H_4\langle^{CH_3}_{SO_3H} + H_2O$$

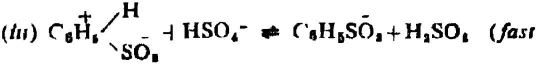
Toluene Sulphuric acid *o*- and *p*- toluene-sulphonic acids

Mechanism of Sulphonation. The commonly accepted mechanism for sulphonation involves the following steps :

(*i*) $2H_2SO_4 \rightleftharpoons H_3\overset{+}{O} + HSO_4^- + SO_3$



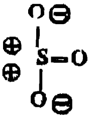
(*ii*) $SO_3 + C_6H_6 \rightleftharpoons \overset{+}{C_6H_5}\langle^{H}_{\overset{-}{SO_3}}$ (*slow*)



(*iii*) $\overset{+}{C_6H_5}\langle^{H}_{\overset{-}{SO_3}} + HSO_4^- \rightleftharpoons C_6H_5\overset{-}{SO_3} + H_2SO_4$ (*fast*)

(*iv*) $C_6H_5\overset{-}{SO_3} + H_3O^+ \rightleftharpoons C_6H_5SO_3H + H_2O$ (*Equilibrium far to the left*)

For sulphonation we commonly use sulphuric acid containing an excess of SO_3. Even if this is not done, it appears that SO_3 formed in step (*i*) is the attacking reagent.



In step (*ii*) the electrophilic reagent, SO_3 attaches itself to the benzene ring to form the intermediate carbocation. Although SO_3 is not positively charged, it is highly electron-deficient, and hence an acid, nevertheless.

In step (*iii*) the carbocation loses a proton to form the resonance-stabilised substitution product, the anion of benzenesulphonic acid which takes a proton to yield benzenesulphonic acid [step (*iv*)] but this being a strong acid, the equilibrium is far to the left.

Sulphonation is a reversible reaction whereas nitration is essentially irreversible. Energy profile for the nitration of benzene is given in Fig. 36·1. Height of the energy barrier on the left is higher than that on the right. The energy of activation, $E_{act(1)}$ leading from the **σ-complex** back to reactants through

$\longleftarrow$

transition state 1 is considerably greater than the energy of activation, $E_{act(2)}$ leading from the σ complex to products through

$\longrightarrow$

transition state 2. Hence in the nitration of benzene once a σ complex is formed the reaction always proceeds further over the lower energy barrier $\underrightarrow{E_{act(2)}}$ to the product nitrobenzene. *Nitration is, therefore, essentially irreversible.*

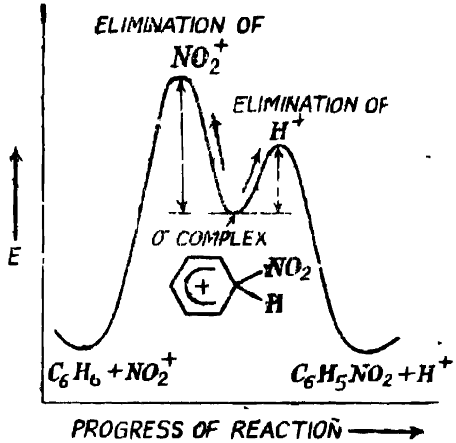


Fig. 36·1—Energy profile diagram for nitration of benzene proceeding through transition states 1 and 2. $\underleftarrow{E_{act(1)}} > \underrightarrow{E_{act(2)}}$

Energy profile for sulphonation of benzene proceeding through transition states 1 and 2 is shown in Fig. 36·2 with energy barrier on either side of the σ complex of roughly the same height.

$\underrightarrow{E_{act(1)}}$ is approximately equal to $\underleftarrow{E_{act(2)}}$. Hence even after the σ complex is formed, the reaction can proceed forward or backward with equal facility. *Sulphonation is, therefore, a reversible reaction.*

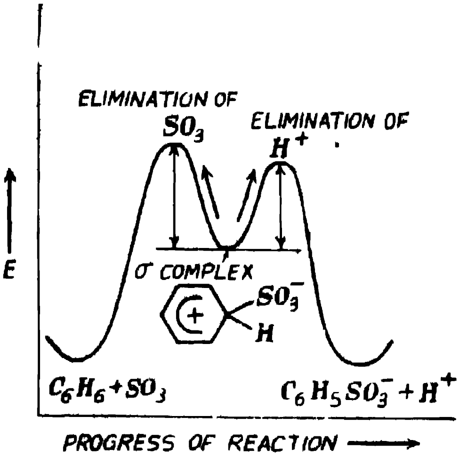
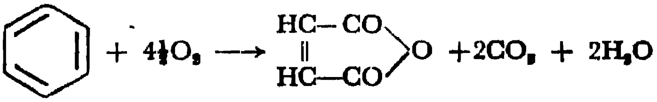
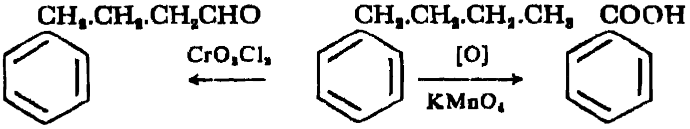


Fig. 36·2—Energy profile diagram for sulphonation of benzene proceeding through transition states 1 and 2 $\underleftarrow{E_{act(1)}}$ and $\underrightarrow{E_{act(2)}}$ are approximately equal.

(4) **Oxidation.** Benzene is oxidised slowly on drastic oxidation with strong oxidising agents, *e.g.*, chromic acid, potassium permanganate to give carbon dioxide and water. It is oxidised to maleic anhydride when its vapour mixed with air is passed over V_2O_5 at 670K.



In the case of homologues of benzene, the side-chain irrespective of its length is oxidised to a carboxyl group. With mild oxidising agents, *e.g.*, chromyl chloride, only the end methyl group is oxidised to aldehyde group. For example, butylbenzene gives benzoic acid and phenylbutyraldehyde respectively.

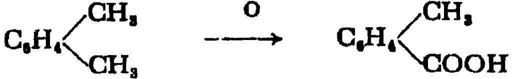


Phenylbutyraldehyde Butylbenzene Benzoic acid

Similarly, toluene on oxidation with mild oxidising agents, *e.g.*, chromyl chloride, gives benzaldehyde while chromic acid or potassium permanganate oxidises toluene directly to benzoic acid.

$$\underset{\text{Benzoic acid}}{C_6H_5.COOH} \xleftarrow{KMnO_4} \underset{\text{Toluene}}{C_6H_5.CH_3} \xrightarrow{CrO_2Cl_2} \underset{\text{Benzaldehyde}}{C_6H_5.CHO}$$

Xylene on oxidation with hot dil HNO_3 gives toluic acid.



$$C_6H_4\begin{matrix}\diagup CH_3\\ \diagdown CH_3\end{matrix} \xrightarrow{O} C_6H_4\begin{matrix}\diagup CH_3\\ \diagdown COOH\end{matrix}$$

o-, *m*-, or *p*- xylene *o*-, *m*-, or *p*-, toluic acid

Side-chain oxidation takes place at the benzylic carbon and as a result of it alkyl groups longer than methyl group are degraded to benzoic acid. The first step is abstraction of benzylic hydrogen by the oxidising agent. Once the oxidation starts at the benzylic carbon, it continues at that site and the benzylic carbon is oxidised to —COOH group ultimately. In the process the remaining carbon atoms of the side-chain are scissored off.

(5) **Reduction.** On reduction with hydriodic acid at 520K or hydrogen under pressure in presence of finely divided nickel at 470K they form cycloalkanes, *e.g.*, benzene gives hexahydrobenzene (*Cyclohexane*).

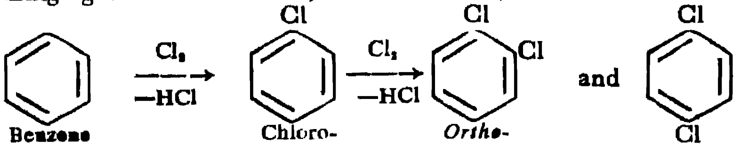
$$\underset{\text{Benzene}}{C_6H_6} + 6[H] \longrightarrow \underset{\text{Cyclohexane}}{C_6H_{12}}$$

(6) **Ozonide formation.** Due to the presence of three double bonds the aromatic hydrocarbons form triozonides by addition of one ozone molecule at each of the double bond.

$$C_6H_6 + 3O_3 \longrightarrow \underset{\text{Benzene triozonide}}{C_6H_6(O_3)_3}$$

(7) **Halogenation.** (*a*) *In cold, dark and in presence of halogen carriers, e.g., iron, iodine.*

(*i*) **In case of Benzene,** one or more hydrogen atoms are replaced by chlorine or bromine (**Substitution**—*Chlorination and Bromination*). Direct iodination is not possible except in presence of oxidising agents like iodic acid, mercuric oxide, etc.

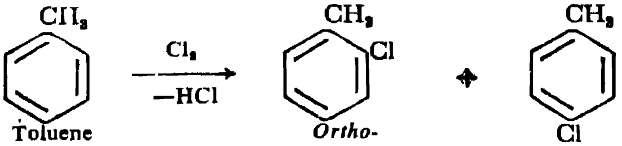


Benzene Chloro-benzene *Ortho-* and *Para-* Dichlorobenzenes

Bromination is similar.

A trihalogen derivative, *e.g.*, $C_6H_3Cl_3$ or $C_6H_3Br_3$ is obtained on further halogenation.

(*ii*) **In case of Toluene or higher homologues,** one or more hydrogen atoms of the nucleus are replaced by chlorine or bromine (**Nuclear Substitution**).

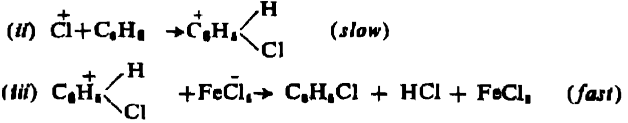


Toluene *Ortho-* and *Para-* Chlorotoluenes

Di- and trichlorotoluenes are obtained on prolonging the passage of chlorine.

Mechanism of Halogenation. The commonly accepted mechanism for aromatic halogenation, as illustrated for chlorination, involves the following steps :

(*i*) $Cl_2 + FeCl_3 \rightarrow FeCl_4^- + \overset{+}{Cl}$



(*ii*) $\overset{+}{Cl} + C_6H_6 \rightarrow \overset{+}{C_6}H_6{<}^{H}_{Cl}$ (*slow*)

(*iii*) $\overset{+}{C_6}H_6{<}^{H}_{Cl} + \overset{-}{FeCl_4} \rightarrow C_6H_5Cl + HCl + FeCl_3$ (*fast*)

Metallic iron commonly used as catalyst is converted into $FeCl_3$ by chlorine.

(*b*) *In Bright Sunlight.* (*i*) **Benzene gives addition products** with chlorine or bromine, *e.g.*,

$$\underset{\text{Benzene}}{C_6H_6} \longrightarrow \underset{\text{Dichloride}}{C_6H_6Cl_2} \longrightarrow \underset{\text{Tetrachloride}}{C_6H_6Cl_4} \longrightarrow \underset{\text{Hexachloride}}{C_6H_6Cl_6}$$

The hexahalides are unstable and decompose when heated alone or with alcoholic potash.

$$\underset{\text{Benzene hexachloride}}{C_6H_6Cl_6} + 3KOH \longrightarrow \underset{\text{Trichlorobenzene}}{C_6H_3Cl_3} + 3KCl + 3H_2O$$

(*ii*) **In case of homologues of Benzene, side-chain substitution** is favoured by *high temperature, light and absence of halogen carriers.* For example, when chlorine is passed through boiling toluene in presence of sunlight, *substitution takes place in the side-chain.*

$$\underset{\text{Toluene}}{C_6H_5CH_3} \xrightarrow[-HCl]{Cl_2} \underset{\text{Benzyl chloride}}{C_6H_5.CH_2Cl} \xrightarrow[-HCl]{Cl_2} \underset{\text{Benzylidene chloride}}{C_6H_5.CHCl_2} \xrightarrow[-HCl]{Cl_2} \underset{\text{Benzylidyne chloride}}{C_6H_5.CCl_3}$$

Mechanism of side-chain Halogenation. Halogenation in the side-chain proceeds by free-radical mechanism just as the halogenation of methane.

$$Cl_2 \xrightarrow{h\nu} 2Cl^{\cdot} \quad \textit{(Free radicals)}$$

$$C_6H_5CH_3 + Cl^{\cdot} \longrightarrow \underset{\text{Benzyl radical}}{C_6H_5CH_2^{\cdot}} + HCl$$

$$C_6H_5CH_2^{\cdot} + Cl_2 \longrightarrow \underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} + \underset{\text{Free radical}}{Cl^{\cdot}}$$

and so on.

Ease of formation of free radicals is in the following order :

allyl or benzyl >3°(tertiary) >2° (secondary) >1° (primary) $>CH_3^{\cdot}>$vinyl.

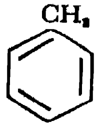
Thus in toluene molecule the position of attack by the halogen is governed by the nature of the attacking particle. Atom (or the free radical) attacks the side-chain whereas the ion attacks the ring.

(8) **Friedel-Crafts Reaction.** This reaction involves the introduction of an alkyl or acyl group into the benzene ring in presence of a catalyst. Different alkylating agents are alkyl halides, alcohol and olefins while acylating agents are acids, acid chlorides, acid anhydrides and esters. Various catalysts used are anhydrous $AlCl_3$, $FeCl_3$, $ZnCl_2$, $SnCl_4$ and BCl_3 (*Lewis acids*).

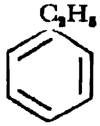
Some of the organic compounds prepared by this reaction are :

(*a*) *Hydrocarbons*

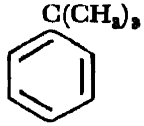
$$CH_3Cl \xrightarrow{AlCl_3} \overset{+}{C}H_3\overset{-}{A}lCl_4 \xrightarrow[-AlCl_3;\ -HCl]{C_6H_6}$$



$$CH_2{=}CH_2 \xrightarrow[\text{HCl (traces)}]{AlCl_3} CH_3\overset{+}{C}H_2\overset{-}{A}lCl_4 \xrightarrow{C_6H_6}$$

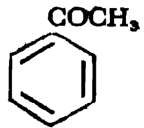


$$(CH_3)_3COH \xrightarrow{BF_3} (CH_3)_3\overset{+}{C} + HO\overset{-}{B}F_3 \xrightarrow{C_6H_6}$$



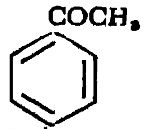
(*b*) *Ketones*

$$\underset{\text{Acetyl chloride}}{CH_3COCl} \xrightarrow{AlCl_3} CH_3\overset{+}{C}O\ \overset{-}{A}lCl_4 \xrightarrow{C_6H_6}$$



Acetophenone

$$\underset{\text{Acetic anhydride}}{(CH_3CO)_2O} \xrightarrow{BF_3} CH_3\overset{+}{C}O\ CH_3COO\overset{-}{B}F_3 \xrightarrow{C_6H_6}$$



Acetophenone

(c) ***Acid chlorides and acids.***

$$\underset{\text{Carbonyl chloride}}{ClCOCl} \xrightarrow{AlCl_3} Cl\overset{+}{C}O\ AlCl_4^- \xrightarrow{C_6H_6} \underset{\text{Benzoyl chloride}}{C_6H_5COCl}$$

$$C_6H_5CO\boxed{Cl\ +\ H}OH \longrightarrow \underset{\text{Benzoic acid}}{C_6H_5COOH} + HCl$$

(d) ***Acid amides.***

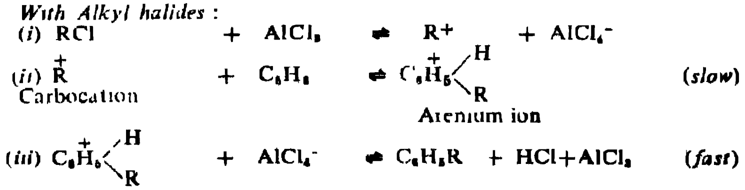
$$\underset{\text{Chloroformamide}}{NH_2COCl} \xrightarrow{AlCl_3} NH_2\overset{+}{C}O\ \overset{-}{AlCl_4} \xrightarrow{C_6H_6} \underset{\text{Benzamide}}{C_6H_5CONH_2}$$

(e) ***Di- and Triphenylmethanes.***

$$2C_6H_6 + CH_2Cl_2 \longrightarrow \underset{\text{Diphenylmethane}}{C_6H_5.CH_2C_6H_5} + 2HCl$$

$$3C_6H_6 + CHCl_3 \longrightarrow \underset{\text{Triphenylmethane}}{(C_6H_5)_3CH} + 3HCl$$

Mechanism of Friedel-Crafts Reaction. It is believed that Friedel-Crafts reactions proceed through the intermediate formation of carbocation or acyl cation.

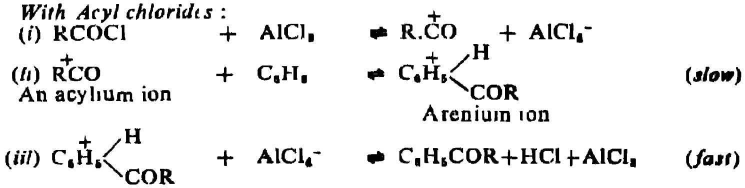


With Alkyl halides :

(i) $RCl + AlCl_3 \rightleftharpoons R^+ + AlCl_4^-$

(ii) $\underset{\text{Carbocation}}{\overset{+}{R}} + C_6H_6 \rightleftharpoons \underset{\text{Arenium ion}}{\overset{+}{C_6H_6}\langle^{H}_{R}}$ (*slow*)

(iii) $\overset{+}{C_6H_6}\langle^{H}_{R} + AlCl_4^- \rightleftharpoons C_6H_5R + HCl + AlCl_3$ (*fast*)



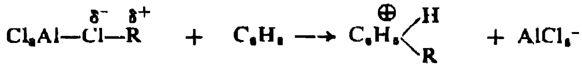
With Acyl chlorides :

(i) $RCOCl + AlCl_3 \rightleftharpoons R.\overset{+}{C}O + AlCl_4^-$

(ii) $\underset{\text{An acylium ion}}{R\overset{+}{C}O} + C_6H_6 \rightleftharpoons \underset{\text{Arenium ion}}{\overset{+}{C_6H_6}\langle^{H}_{COR}}$ (*slow*)

(iii) $\overset{+}{C_6H_6}\langle^{H}_{COR} + AlCl_4^- \rightleftharpoons C_6H_5COR + HCl + AlCl_3$ (*fast*)

In the other mechanism, the electrophile is the alkyl group in the polar complex between $AlCl_3$ and the alkyl halide

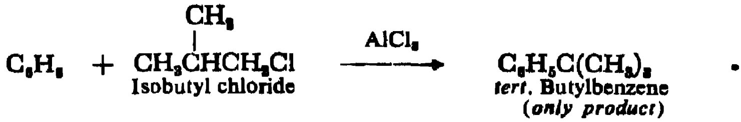


$$Cl_3Al-\overset{\delta^-}{Cl}-\overset{\delta^+}{R} + C_6H_6 \longrightarrow \overset{\oplus}{C_6H_6}\langle^{H}_{R} + AlCl_4^-$$

The less stable (1°) carbocation rearranges by a 1, 2-shift to a more stable (2° or 3°) carbocation. For example,

$$\underset{}{C_6H_6} + \underset{n\text{-Propyl chloride}}{CH_3.CH_2.CH_2Cl} \xrightarrow{AlCl_3} \underset{\substack{n\text{-Propylbenzene}\\ 31\text{-}35\%}}{C_6H_5.CH_2CH_2CH_3} \text{ and } \underset{\substack{\text{Isopropylbenzene}\\ 65\text{-}69\%}}{C_6H_5CH(CH_3)_2}$$

n-Propylbenzene is obtained mainly if the reaction is carried out in cold.



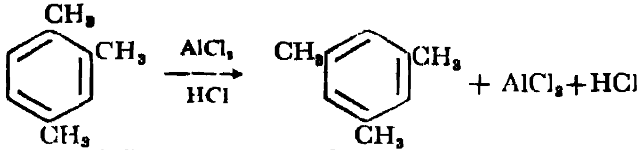
$$C_6H_6 + \underset{\text{Isobutyl chloride}}{CH_3\overset{\overset{CH_3}{|}}{C}HCH_2Cl} \xrightarrow{AlCl_3} \underset{\substack{tert.\text{ Butylbenzene}\\ (only\ product)}}{C_6H_5C(CH_3)_3}$$

Limitations of Friedel-Crafts Reaction. There are several restrictions which limit the usefulness of the Friedel-Crafts reaction. For example, (*i*) Aryl and vinyl halides which do not form carbocations easily, cannot be used as halide component.

(*ii*) Polyalkylation takes place quite often. After the introduction of one alkyl group (an activating group) the ring gets activated for further substitution. Friedel-Crafts acylation does not suffer from this defect since acyl or aroyl group, being deactivating group, does not facilitate further substitution.

(*iii*) Carbocations formed during the reaction rearrange to yield more stable carbocations as shown above.

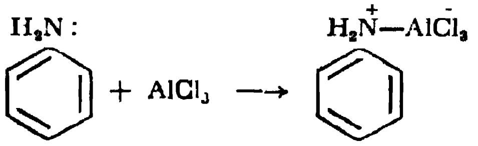
(*iv*) It is often accompanied by rearrangement of alkyl group attached to the nucleus. For 1, 2, 4-Trimethylbenzene rearranges to give mesitylene in Friedel-Crafts reactions.



1, 2, 4-Trimethylbenzene Mesitylene

(*v*) The presence of an electron-withdrawing group (*m*-orienting group) in the ring hinders or inhibits the Friedel-Crafts reaction, *e.g.*, nitrobenzene and acetophenone do not undergo this reaction. On the other hand, if an *o*-, *p*-orienting, strong activating group (electron releasing group) is present in either of the above two compounds, reaction can take place. For example, *o*-nitroanisole can undergo this reaction.

Presence of NH_2, NHR and NR_2 groups also inhibits the reaction. This is because these groups become powerful electron withdrawing groups by reacting with Lewis acid when compounds containing these are placed in Friedel-Crafts reaction mixtures.



Aniline Lewis acid Does not undergo a Friedel-Crafts reaction

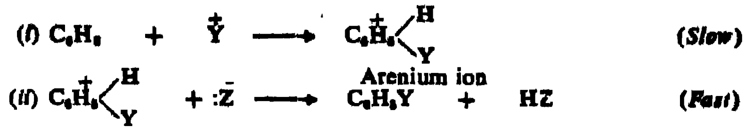
(9) **Mercuration.** Benzene or its homologue is heated (360-430K) with mercuric acetate for one or more hours when one hydrogen atom is replaced by acetoxy-mercuric group.

$$C_6H_6 + (CH_3COO)_2Hg \longrightarrow \underset{\substack{\text{Acetoxymercuribenzene}\\ \text{or Phenylmercury acetate}}}{C_6H_5—Hg.OOCCH_3} + CH_3COOH$$

Aromatic mercuriated compounds are increasing in importance in medicine and in preparation of other compounds.

Mechanism of Electrophilic aromatic substitution (a summary)

From the above discussion electrophilic aromatic substitution reactions seem to proceed by a single mechanism whatever the particular reagent involved. This can be summarized for the regent YZ as follows :



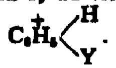
$$(i)\ C_6H_6 + \overset{+}{Y} \longrightarrow C_6\overset{+}{H}_6{<}^{H}_{Y} \qquad \textit{(Slow)}$$

Arenium ion

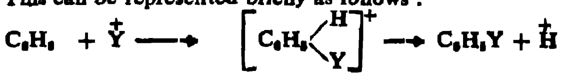
$$(ii)\ C_6\overset{+}{H}_6{<}^{H}_{Y} + \bar{:Z} \longrightarrow C_6H_5Y + HZ \qquad \textit{(Fast)}$$

The two essential steps involved in the substitution are :

(*i*) Attack by an electrophilic reagent upon the ring to form a carbocation (arenium ion), $C_6\overset{+}{H}_6{<}^{H}_{Y}$.



(*ii*) Abstraction of hydrogen ion from the carbocation by some base. This can be represented briefly as follows :



$$C_6H_6 + \overset{+}{Y} \longrightarrow \left[C_6H_6{<}^{H}_{Y}\right]^{+} \longrightarrow C_6H_5Y + \overset{+}{H}$$

In electrophilic aromatic substitution reactions, the electrophile may be a positive ion, *e.g.*, $^{+}NO_2$ (nitronium ion) in the nitration or it may be a species that bears only a partial positive charge, *e.g.*, in halogenation reactions the electrophiles are halogen-Lewis acid complexes in which halogen is partially positive, *e.g.*,

$$\overset{\delta+}{:\ddot{\underset{..}{Br}}}—\overset{\delta-}{\ddot{\underset{..}{Br}}}FeBr_3 \text{ (wherein } FeBr_3 \text{ is Lewis acid)}$$

Electrophile may also be a neutral Lewis acid, *e.g.*, in sulphonation reactions it is usually SO_3 (a Lewis acid).

INDIVIDUAL MEMBERS

4. **Benzene, C_6H_6.**—Benzene was first isolated by Faraday in 1825 from oil condensed in cylinders of compressed illuminating gas obtained by the destructive distillation of whale oil. Hofmann pointed out in 1845 that benzene was found in coal-tar which is still a commercial source of benzene. Large quantities of benzene and its homologues are prepared in the USA by cracking petroleum.

Preparation. Benzene can be prepared by any of the general methods given before. It is, however, conveniently prepared in the laboratory by heating a mixture of sodium benzoate (20 g) and soda lime (30 g) in a distillation flask connected to Liebig's condenser and receiver. Benzene distils over. It is dried over anhydrous calcium chloride and redistilled.

Commercial preparation of Benzene from Coal-tar. Coal-tar is subjected to fractional distillation and its first fraction, called *Light oil*, is washed successively with cold concentrated sulphuric acid (which removes basic impurities, *e.g.*, pyridine and some thiophene), water, dilute sodium hydroxide solution (which removes acidic impurities, *e.g.*, phenol, cresol) and water. It is finally washed with water, dried and subjected to fractional distillation again.

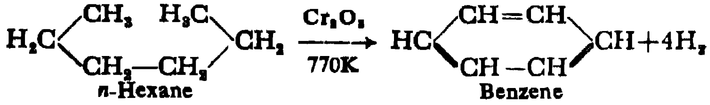
The fraction (350-380K) called 90% *Benzol* or the fraction (380-410K) called 50% *Benzol* are worked for the recovery of benzene present in them. Benzol is distilled fractionally and the fraction passing between 353-355K is collected. This is then cooled in freezing mixture and the crystals of benzene separated from the impurities. The process of distillation and freezing is repeated until it boils off at 353-354K. It is pure benzene containing some thiophene (C_4H_4S, having b.p. and m.p. almost the same as that of benzene) as impurity.

This is repeatedly washed with cold concentrated sulphuric acid until it gives no blue colour with a trace of isatin in concentrated sulphuric acid (shows absence of thiophene). The product is washed, dried and redistilled.

A better means of separation of thiophene is to reflux benzene with aqueous mercuric acetate when thiophene is mercurated and benzene remains unaffected. The two can now be separated.

Commercially thiophene is removed by heating benzene with hydrogen under pressure at about 670K in presence of a catalyst. Thiophene gives *n*-butane and hydrogen sulphide.

Commercial preparation from Petroleum. Benzene is also manufactured by cyclization of hexane obtained from petroleum. Vapours of alkanes under pressure are passed over a chromium catalyst (Cr_2O_3 supported on alumina) heated to 770K.



Synthesis. Benzene was first synthesised by Berthelot in 1873 by passing acetylene through red-hot tube.

$$3C_2H_2 \rightarrow C_6H_6$$

Properties : Physical. Benzene is a colourless liquid (m.p. 278·5K ; b.p. 353K) with a characteristic smell. It is insoluble in water but miscible in all proportions with alcohol and ether. It is a good solvent itself for fats, resins, sulphur, iodine, etc.

Chemical. Chemical properties of benzene have already been discussed under general properties of benzene and its homologues.

Uses. Benzene is used :

(*i*) As a solvent for fats, resins, etc.

(*ii*) In dry-cleaning.

(*iii*) As a motor fuel under the name "benzol".

(*iv*) For the manufacture of styrene (used in synthesising plastics and rubber), phenol (used in making dyes, plastics, etc.), aniline (used for making dyes, drugs, etc.), isopropylbenzene (added to gasoline to raise its octane number), nylon, detergents, insecticides (DDT, $C_6H_6Cl_6$, etc.) maleic anhydride, solvents, etc.

5. **Constitution of Benzene.**—(*i*) *Molecular formula* of benzene as calculated from its combustion and vapour density data is C_6H_6.

(*ii*) *Unsaturated Appearance.* Low proportion of hydrogen to carbon (*c.f.* C_6H_{14}, hexane—corresponding paraffin) suggests that benzene is an unsaturated compound like ethylene or acetylene.

(*iii*) *Behaves like a Saturated Compound.* Like other unsaturated compounds benzene does not readily decolorise bromine water or alkaline potassium permanganate (*Baeyer's reagent*), *i.e.*, it behaves like a saturated compound.

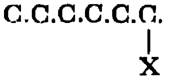
(*iv*) *Presence of three Double Bonds* is indicated by the fact that in the presence of sunlight (*or ultraviolet light*) it adds six chlorine atoms to give $C_6H_6Cl_6$.

It is also shown by the fact that benzene forms a *triozonide* $C_6H_6(O_3)_3$.

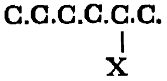
(*v*) *Inference.* From the above we infer that benzene is an unsaturated compound having three double bonds but behaves like a saturated compound ordinarily. This suggests a structure for benzene entirely different from open-chain unsaturated compounds.

(*vi*) *Further Evidence.* The following facts support the above view :

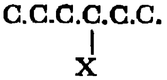
(*a*) Benzene forms only one mono-substitution product, *e.g.*, only one chlorobenzene is known. A straight-chain formula, if assigned to benzene, would give three or even more mono-substitution products as indicated below :



$$\text{C.C.C.C.C.}\underset{\underset{\text{X}}{|}}{\text{C}}.$$



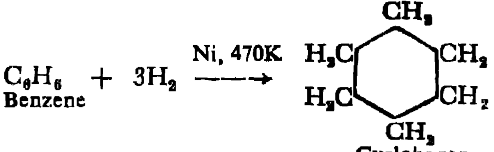
$$\text{C.C.C.C.}\underset{\underset{\text{X}}{|}}{\text{C}}\text{.C.}$$



$$\text{C.C.C.}\underset{\underset{\text{X}}{|}}{\text{C}}\text{.C.C.}$$

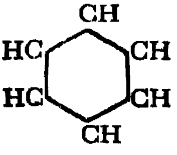
(*b*) Reaction of benzene, *e.g.*, Nitration, Sulphonation, Friedel-Crafts reaction, etc., are either unknown or uncommon with open chain unsaturated hydrocarbons.

(*c*) On reduction with hydrogen under pressure in presence of finely divided nickel at 470K, it gives cyclohexane which indicates a ring structure for benzene.

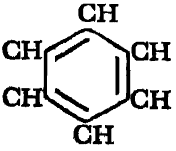


Cyclohexane

(*vii*) *Kekule's Formula.* Keeping all these facts in view Kekule suggested in 1865 a ring formula for benzene wherein he assumed that six carbon atoms were lying at the six corners of a regular hexagon and hydrogen atoms were equally divided among these, *i.e.*, each carbon atom carries one hydrogen atom--*see* the formula given in margin.



To account for the fourth valency of each carbon atom, he assumed a system of alternate double and single bonds as shown in the margin.

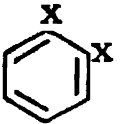


*Main defects of the *Kekule's formula were* :

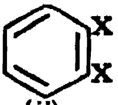
(*a*) It could not explain the saturated nature of benzene.

(*b*) Two ortho-disubstitution products of benzene were possible as (*i*) and (*ii*) given below :

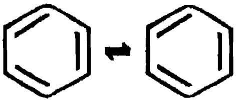
*** Kekule von S. Friedrich August (1829-96)—German chemist who is famous for his theory of the ring structure of organic compounds. His formula for benzene was the result of his dreaming of a serpent catching its own tail.**



(*i*)

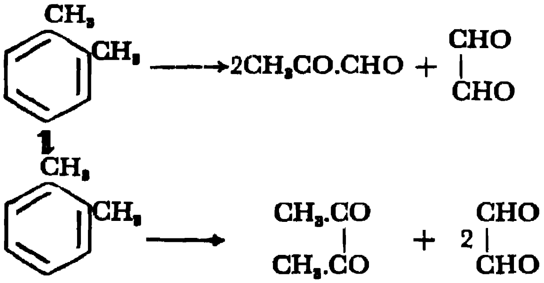


(*ii*)



To remove the second defect, Kekule assumed the double bonds to be in a rapid state of oscillation, which leaves no difference between the two ortho disubstitution products (*i*) and (*ii*) given above.

In 1932 Levine and Cole subjected *o*-xylene to ozonolysis and obtained glyoxal, methylglyoxal and dimethylglyoxal. These could not be obtained unless two forms of *o*-xylene were present.

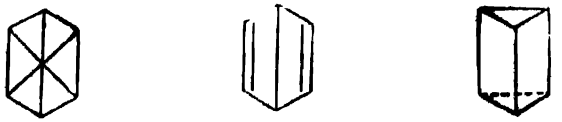


(Closed chain ruptures at the position of double bonds to yield these products.)

In this way the authors supported Kekule's oscillation (tautomeric) hypothesis.

(*viii*) *Some other formulae.* Kekule's formula did not explain the peculiar behaviour of double bonds in benzene. **Claus** (1867), therefore, introduced his diagonal formula and **Dewar** (1867) suggested another formula. To explain the fact that there was only one ortho-disubstitution product, **Ladenburg** (1869) proposed his prism formula stating that the six carbon atoms lie at the six corners of a regular prism, the edges of which denote linkages.

Out of these Dewar's formula is not symmetrical and was, therefore, not acceptable. The prism formula had no double bonds and thus did not account for the addition products of benzene. Moreover, X-ray spectra of benzene shows regular hexagonal structure. In all the three formulae length of some of the bonds is too much and is a point of weakness rather than strength.



(*a*) Claus diagonal formula

(*b*) Dewar's formula

(*c*) Ladenburg's prism formula

Fig. 36·3—Some other formulae for benzene.

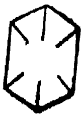
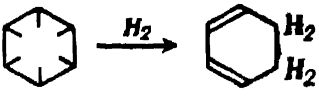


Fig. 36·4—Armstrong-Baeyer's centric formula.

(*ix*) ***Armstrong-Baeyer's Centric formula*** (1887). According, to this, the fourth valency of each carbon atom is represented as directed towards the centre of the ring but not actually linked to opposite neighbour in the Claus formula. The centric bond is only potential, not real. By mutual action there is a condition of equilibrium between these bonds and accounts for the aromatic properties.

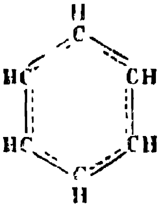
When benzene is converted into dihydrobenzene by some indirect method (direct hydrogenation is not possible), the condition of equilibrium is destroyed and two double bonds appear. The product behaves as a typical diolefin.



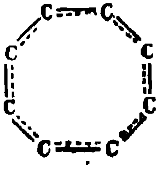
Benzene **Dihydrobenzene**
(*Cyclohexadiene*)

The centric formula is, however, unsatisfactory as it does not explain the stability of the ring or the behaviour of the polynuclear hydrocarbons.

(*x*) *Thiele's formula.* Thiele applied his theory of partial valency to the benzene problem and suggested the following formula for benzene :



Thiele's formula for benzene



Cyclooctatetraene with conjugated double and single bonds.

This formula dispenses with Kekule's oscillation hypothesis. Herein there is no difference between 1 : 2 and 1 : 6 position. At the same time there being no free valencies it behaves as a saturated compound.

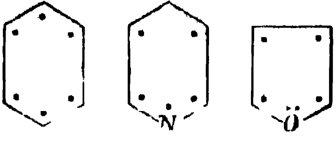
As suggested by Thiele, if aromatic character is due to symmetrical conjugation of the benzene ring then cyclooctatetraene should also exhibit aromatic character but it has a typical unsaturated character.

The approach even today is still an attempt to account for the fourth valency of each carbon and define the aromatic character of benzene.

6. Aromaticity or the Aromatic Character.—Properties of benzenoid compounds were found to be very much different from those of analogous aliphatic and alicyclic compounds ; for example, ease of substitution in benzene and its derivatives in spite of its unsaturated nature, weakly basic properties of aromatic amines, acidic nature of phenols. This unique character of benzenoid compounds was termed Aromaticity or Aromatic character. Chemists have been trying to seek an explanation for this and in consequence to define aromaticity.

Out of the number of theories put forward, the following three are important :

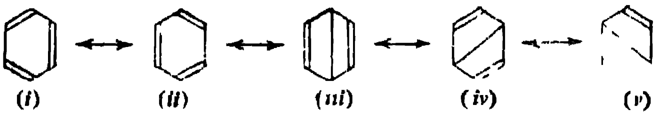
(a) **Aromatic Sextet theory.** It was originally suggested by Bomberger (1891) and later on modified according to electronic theory by Robinson (1925). Ingold (1928) and Huckel (1930). According to this, there are six electrons in excess than are necessary to link six carbon atoms. These six electrons form a closed group responsible for the aromatic properties. This group is present in heterocyclic compounds also and is responsible for the aromatic character shown by them. Aliphatic compounds differ from aromatic compounds for want of this group.



Benzene Pyridine Furan
All of these possess a group of six electrons.

(b) **Valence bond theory of aromaticity.** X-ray analysis and other experimental results have established that benzene is a flat hexagon with all its hydrogen atoms lying in the plane of the ring and each C—C—H valency angle being 120°. All C—C bond lengths are the same (=1·397Å). This suggests that each bond is partly a single bond (bond length 1·54Å) and partly a double bond (bond length 1·33Å).

Planar structure and 120° bond angle is explained on the assumption that carbon atoms in benzene ring are sp^2 hybridised. Shortening of bond length and the aromatic properties of benzene are explained on the basis of resonance. According to this theory, benzene is believed to be a resonance hybrid of the following structures :



Kekule structures contribute about 80% to resonance. Further more, since the two Kekule structures are equivalent, the stability of

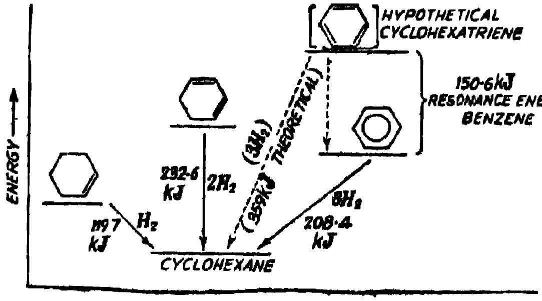


Fig. 36·5—The actual molecule of benzene is 150·6 kJ per molecule more stable than the hypothetical cyclohexatriene. In order to observe normal alkene reactions of benzene, we would have to expend this additional amount of energy to localise the π electrons. Thus, more energy, usually in the form of higher reaction temperatures, is required for reactions of benzene than for similar reactions of non-aromatic alkenes.

the resulting resonance hybrid is very high. Resonance energy of benzene (=150·6 kJ mol^{-1}) being high makes benzene relatively stable in comparison with aliphatic unsaturated compounds and hence its '*aromatic character*'.

Thermochemical calculations show that introduction of three double bonds in cyclohexane to get benzene should be accompanied by heat change of about 359 kJ mol^{-1}, but the experimental value is only 208·4 kJ mol^{-1}. The difference between these two values (=150·6 kJ mol^{-1}) is the resonance energy of benzene. Thus benzene contains less energy than expected and is, therefore, more stable than expected.

Resonance gives each C—C bond in benzene some double bond character. The C—C bond length in benzene has been found to be 1·397 Å which lies between that of a single bond, C—C in ethane (=1·54 Å) and that of a double bond, C=C in ethylene (=1·33 Å). Further since all the six C—C bonds in benzene are the same, it shows the symmetrical nature of the benzene ring.

Further evidence. Evidence that the benzene ring is planar has been obtained from studies of X-ray analysis, dipole moments, Raman spectra and electron diffraction photographs of benzene vapour. In an X-ray diffraction photograph of a molecule of hexamethylbenzene $C_6(CH_3)_6$ shown in Fig. 36·6, six black spots arranged in hexagon are six carbon atoms of benzene ring and the outer spots are carbon atoms of six methyl groups attached to these six carbon atoms. This offers a visible proof of the hexagonal arrangement of the carbon atoms.

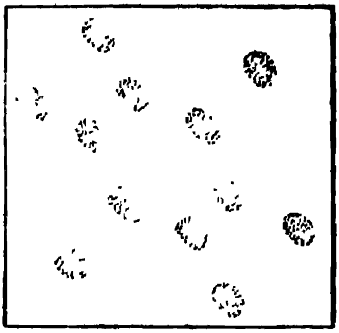
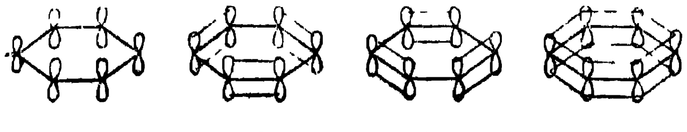


Fig. 36·6—X-ray diffraction photograph of hexamethylbenzene.

(c) The Molecular Orbital Theory of Aromaticity.

In terms of the molecular orbital theory benzene, as shown by spectroscopic studies and X-ray analysis, is a regular flat hexagon (angle=120°) with all the six carbon atoms lying in the same plane and each C—C—H angle also being 120°. *Thus each carbon atom is in a state of trigonal hybridisation (sp^2 hybridisation).* Thus in benzene molecule there are six *sigma* C—H bonds, six *sigma* C—C bonds and six $2p_z$ orbitals (one of each carbon atom) which are all parallel and perpendicular to the plane of the ring [*see* Fig. 36·7 (*i*)].

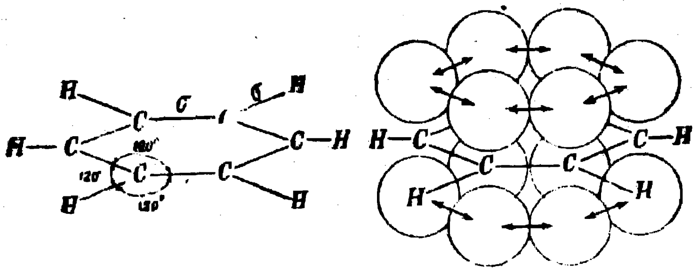


(*i*) (*ii*) (*iii*) (*iv*)

Fig. 36·7—Structure of benzene in terms of molecular orbital theory.

These orbitals can overlap in two equally good ways as shown in (*ii*) and (*iii*) above. Each $2p_z$ orbital, however, overlaps the neighbour

equally. All the six orbitals are, therefore, completely delocalised and form a molecular orbital embracing all the six carbon atoms as shown in Fig. 36·7(*iv*).



(*a*) (*b*)

Fig. 36·8—Benzene molecule. (*a*) Only σ bonds are shown, (*b*) *p*-orbitals overlap to form π bonds and π electron clouds are present above and below the plane of the ring.

Thus there are two continuous hexagonal electron clouds, one lying above and the other below the plane of the atoms [*see* Fig. 36·8(*b*)].

The overlapping of the *p*-orbitals in both directions and the resulting participation of each electron in several bonds is equivalent to our earlier description of benzene as a resonance hybrid of several structures. *This delocalization of π electrons results in stronger bonds and more stable molecule.* For this reason the term *delocalization energy* is frequently used instead of *resonance energy*.

The orbital approach reveals the importance of the planarity of the benzene ring. Since the trigonal sp^2 bond angles just fit the 120° angles of a regular hexagon, the ring is flat and this flatness permits the overlapping of the *p*-orbitals in both directions resulting in stabilisation due to delocalization of *p*-orbitals.

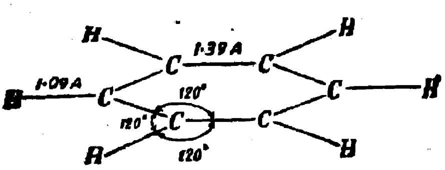


Fig. 36·9—Shape and size of benzene molecule.

In the benzene molecule each C—C bond length = 1·397Å, each C—H bond length = 1·09Å. The benzene ring is completely flat and the bond angles are 120°.

Chemical properties of benzene are just what we would expect of this structure. Despite delocalization, the π electrons are more loosely held than the σ electrons and are readily available to an electrophile. Benzene ring thus serves as a source of electrons for electrophilic (acidic) reagents. Since benzene ring is stabilised by resonance, these reactions lead to substitution in which aromatic character of the benzene ring is preserved.

Aromatic Character and the Huckel's (or 4n+2) Rule. We have defined aromatic compounds as those which resemble benzene. But there are many substances called aromatic, yet bearing little resemblance to benzene superficially. Hence we must know as to which properties of benzene must a compound possess before we speak of it as being aromatic. For this let us study what properties do all aromatic compounds have in common.

(*i*) These are ***highly unsaturated*** compounds but resistant to addition reactions generally characteristic of unsaturated compounds.

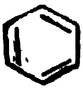
(*ii*) They are ***unusually stable*** as shown by their low heats of hydrogenation and low heats of combustion. Heat of hydrogenation of benzene is only 208·4 kJ mol^{-1} against that of cyclohexatriene =359·8 kJ mol^{-1}. Heat of combustion of benzene is only 3378 kJ mol^{-1} against that of cyclohexatriene=3447 kJ mol^{-1}.

(*iii*) Aromatic compounds *undergo electrophilic substitution* reactions like those of benzene.

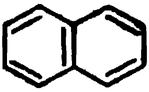
(*iv*) These are *cyclic** compounds containing generally *five-, six-, or seven-member rings* and are found to have *flat molecules.*

From the theoretical standpoint, a compound is aromatic only when it has a molecule containing cyclic clouds of delocalized π electrons above and below the plane of the molecule. Moreover, the π clouds must contain a total of $(4n+2)$ π electrons. Thus we find that delocalization alone is not enough. There must be a particular number of π electrons—2 or 6, or 10, etc. This requirement called the $4n+2$ *rule* or *Huckel's rule* is based on quantum mechanics.

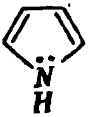
Benzene has six π electrons, the aromatic sextet. Naphthalene is made up of two fused benzene rings while anthracene and phenanthrene are made up of three fused benzene rings. Besides these there are some heterocyclic compounds which are clearly aromatic, *e.g.*, pyridine, pyrrole, thiophene and furan. Each one of these has the aromatic sextet



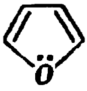
Benzene
(6 π electrons)



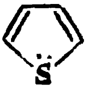
Naphthalene
(10 π electrons)



Pyrrole



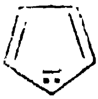
Furan



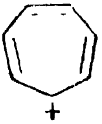
Thiophene

(each contains 6 π electrons)

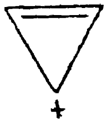
In addition to these neutral molecules there are a number of monocyclic ions which are aromatic according to Huckel's rule. For example,



Cyclopentadienide
anion
(6 π electrons)



Cycloheptatrienyl
cation
(6 π electrons)



Cyclopropenyl
cation
(2 π electrons)

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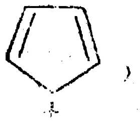
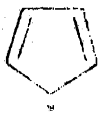
* Monocyclic compounds having alternate double and single bonds are given a general name Annulenes. The ring size of an annulene is indicated by a number in brackets. For example benzene is [6] annulene and cyclooctatetraene is [8] annulene. However, these names are often used only for conjugated rings of 10 or more carbon atoms.

Those ions or radicals which do not satisfy Huckel's rule are not aromatic. For example



Cyclopentadienyl
cation
(5 π electrons)



Cyclopentadienyl
radical
(5 π electrons)

[Both Non-aromatic]

Aromaticity may thus be defined as follows : *A monocyclic compound is aromatic if it has a reasonably planar cyclic structure, has (4n+2) π-electrons and possesses unusual stability due to delocalisation of π-electrons.*

7. Toluene, Methylbenzene or Phenylmethane, $C_6H_5CH_3$.—Toluene was obtained by the dry distillation of *Tolu balsam* whence it derives its name. It is commercially known as toluol.

Preparation. It can be prepared by any of the general methods of preparation of homologues of benzene. It is, however, obtained commercially :

(*i*) *From coal-tar.* 50% benzol is obtained by the fractional distillation of light oil—a fraction of coal-tar distillation as given on page *2 474*. It contains a large percentage of toluene which can be separated by subjecting it to fractional distillation. The fraction distilling over between 381-383K, which is toluene, is collected.

(*ii*) *By catalytic dehydrogenation of n-heptane or methylcyclohexane (both obtained from petroleum).*

$$\underset{n\text{-heptane}}{CH_3(CH_2)_5.CH_3} \rightarrow \underset{\text{Toluene}}{C_6H_5.CH_3} + 4H_2$$

Properties. Toluene is a colourless liquid (b.p. 384K) with benzene-like odour. It is insoluble in water but soluble in alcohol and ether. Its chemical properties have already been discussed (*see* pages *2·479-2·486*).

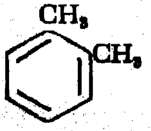
Uses. (*i*) Toluene is a commercial solvent.

(*ii*) It is used in the manufacture of explosives (*e.g.*, TNT), drugs and dyestuffs.

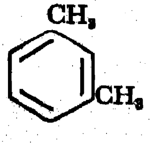
(*iii*) It finds use in the manufacture of saccharine and printing inks.

(*iv*) With petrol and benzene, toluene is used as an antifreeze.

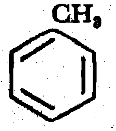
8. Xylene, Dimethylbenzene, $C_6H_4(CH_3)_2$.—Xylene shows position isomerism and is isomeric with ethylbenzene. The four isomerides represented by the molecular formula C_8H_{10} are :



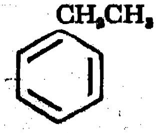
o-Xylene
(b.p. 417K)



m-Xylene
(b.p. 412K)



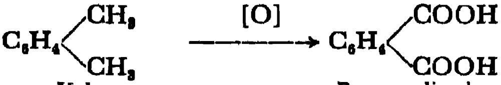
p-Xylene
(b.p. 411K)



Ethylbenzene
(b.p. 409K)

Xylenes can be prepared using general methods of preparation of homologues of benzene. These are all colourless liquids insolube in water but soluble in alcohol and ether.

On oxidation *o*-, *m*-, and *p*-xylenes give *o*-, *m*-, and *p*-benzene-dicarboxylic acids respectively.



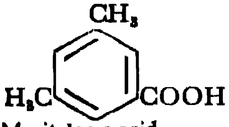
$$C_6H_4(CH_3)_2 \xrightarrow{[O]} C_6H_4(COOH)_2$$

Xylene Benzenedicarboxylic acid

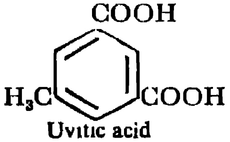
Xylenes are used in the manufacture of lacquers and as solvent for rubber. Their amino-derivatives are used in the manufacture of dyes.

9. **Mesitylene, 1 : 3 : 5-Trimethylbenzene, $C_6H_3(CH_3)_3$.**—Mesitylene occurs in coal-tar. It is, however, prepared by condensation of acetone (by distilling it with concentrated sulphuric acid) or by polymerisation of propyne in presence of conc. H_2SO_4.

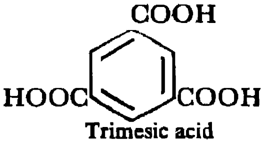
Properties. It is a colourless, pleasant-smelling liquid (b.p. 337K). On oxidation with dilute nitric acid the three methyl groups attached to the nucleus are successively replaced by —COOH groups and give



Mesitylenic acid



Uvitic acid



Trimesic acid

10. **Cymene, $CH_3.C_6H_4.CH(CH_3)_2$. *p*-Methylisopropylbenzene.**—It occurs in oil of thyme and eucalyptus oil. It is related to camphor and other terpenes. Cymene (b.p. 450K) can be prepared by heating turpentine oil.

11. **Cumene, Isopropylbenzene, $C_6H_4.CH(CH_3)_2$.**—It is a liquid (b.p. 426K) and occurs in coal-tar.

12. **Styrene, Phenylethylene, Vinylbenzene, $C_6H_5.CH{=}CH_2$.**—It occurs in coal-tar and storax (a balsam). It can be prepared—

(*i*) ***By dehydration of 1-phenylethanol with sulphuric acid.***

$$C_6H_5CHOH.CH_3 \xrightarrow[-H_2O]{H_2SO_4,\ Heat} \underset{\text{Styrene}}{C_6H_5CH{=}CH_2}$$

(*ii*) ***By heating 2-phenylethanol with alkali.***

$$C_6H_5CH_2.CH_2OH \longrightarrow C_6H_5CH{=}CH_2+H_2O$$

(*iii*) ***By heating cinnamic acid with a little quinol (Laboratory method).***

$$C_6H_5CH{=}CH.COOH \longrightarrow C_6H_5CH{=}CH_2+CO_2$$

A small quantity of liquid is placed in the receiver to prevent polymerisation of styrene.

(*iv*) ***By catalytic dehydrogenation of ethylbenzene (Manufacture).***

$$C_6H_5CH_2.CH_3 \xrightarrow{ZnO,\ 900K} C_6H_5.CH{=}CH_2+H_2$$

Ethylbenzene is prepared by Friedel-Crafts reaction.

$$C_6H_6+CH_2{=}CH_2 \xrightarrow[HCl]{AlCl_3} C_6H_5CH_2.CH_3$$

Properties. It is a colourless liquid (b.p. 418K). With bromine it gives the dibromide and is readily reduced to ethylbenzene.

$$C_6H_5CH{=}CH_2+Br_2 \longrightarrow \underset{\text{Styrene dibromide}}{C_6H_5CHBr.CH_2Br}$$

It polymerises slowly to metastyrene (a solid) on standing and rapidly when exposed to sunlight or in presence of sodium.

Styrene in used in the manufacture of plastics and synthetic rubber.

13. Comparative Study of Benzene and Toluene.

Benzene	Toluene
Points of Similarity :	
(*i*) **Nitration.** With concentrated nitric acid+concentrated sulphuric acid benzene gives mono-, di- and trinitrobenzene.	Toluene on nitration gives *mono* and trinitrotoluene.
(*ii*) **Sulphonation.** With hot concentrated sulphuric acid it gives benzenesulphonic acid while with oleum it yields benzene-*m*-disulphonic acid.	Gives *o*- and *p*-toluenesulphonic acid with hot concentrated sulphuric acid.
(*iii*) **Halogenation in presence of halogen carriers in cold and dark.**	
Substitution in the nucleus gives mono-, di- and trichloro- or tribromobenzene.	Substitution takes place in the nucleus to give *o*- and *p*- chloro- or bromo-toluene.
(*iv*) **Friedel-Crafts Reaction.** *Reaction with halogen derivatives in presence of anhydrous aluminium chloride.*	
Gives higher homologues.	Gives higher homologues.
Points of Distinction .	
(*i*) **Halogenation in sunlight.** Benzene in cold and sunlight gives addition products, *e g.*, $C_6H_6Cl_2$, $C_6H_6Cl_4$ and $C_6H_6Cl_6$	Boiling toluene in sunlight gives side-chain substitution products, *e.g.*, $C_6H_5CH_2Cl$, $C_6H_5CHCl_2$ and $C_6H_5CCl_3$.
(*ii*) **Oxidation.**	
Benzene is quite stable and is oxidised only on drastic treatment.	Toluene is easily oxidised to benzaldehyde (with CrO_2Cl_2) or benzoic acid (with $KMnO_4$, etc)

TEST YOUR UNDERSTANDING

1. From the following figure depicting heats of hydrogenation of benzene, cyclohexadiene and cyclohexene, determine the ΔH values of the following reactions .

(*a*) Benzene$+H_2 \longrightarrow$ 1, 3-cyclohexadiene.

(*b*) 1, 3-cyclohexadiene$+H_2 \longrightarrow$ cyclohexene.

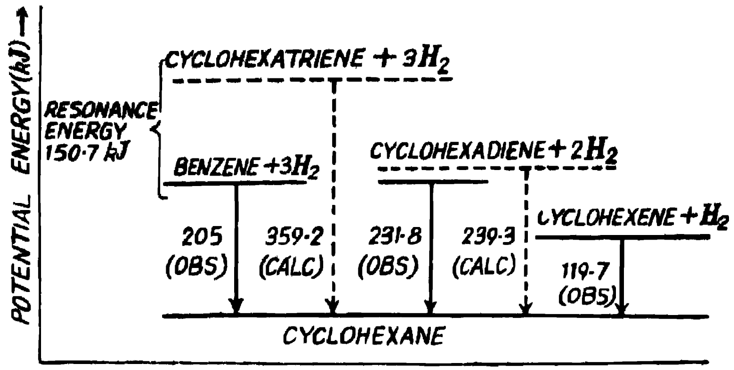


Fig. 36·9.

2. Knowing that in the heat of combustion of a compound there is definite characteristic contribution by each kind of bond shown below :

C—H bond=225·9 kJ. C=C bond=491·2 kJ.

C—C bond=206·3 kJ. (*cis-1, 2, disubstituted*)

Calculate the heat of combustion of cyclohexatriene and compare it with the measured value of 330·2 kJ for benzene.

3. Nitration by nitric acid alone is believed to proceed by the same mechanism as nitration with acid mixture. Write down the generation of NO_2^+ ion from nitric acid alone.

4. How do you account for the fact that benzene in the presence of $AlCl_3$ reacts :

(*a*) with *n*-propyl bromide to give isopropylbenzene, and

(*b*) with neopentyl bromide to yield *tert*-pentylbenzene.

5. How can you get ethylbenzene from :

(*a*) benzene and ethanol ; (*b*) acetophenone ;

(*c*) styrene $C_6H_5CH{=}CH_2$; and (*d*) $C_6H_5.CHOH.CH_3$?

QUESTIONS

Essay Type:

1. How are benzene and toluene obtained from coal-tar ? How does toluene react with (*a*) chlorine, (*b*) nitric acid, (*c*) sulphuric acid and (*d*) alkaline permanganate ? (*Kerala B.Sc. 1973*)

2. What is the action of (*a*) ozone, (*b*) nitric acid, and (*c*) sulphuric acid on benzene ?

Discuss the constitution of benzene. (*Kerala B.Sc. 1972*)

3. How is toluene obtained on a large scale ? From toluene how would you prepare (*a*) benzal chloride, (*b*) benzaldehyde, (*c*) *o*-chlorotoluene ? (*Agra B.Sc. 1973*)

4. (*a*) Give the mechanism of the Friedel-Crafts reaction. (*b*) What method is employed for generation of the electrophile in each of the following reactions :

(*i*) Halogenation, (*ii*) Nitration and (*iii*) Sulphonation. (*Delhi B.Sc. 1977*)

5. Give two reactions for the preparation of toluene. What happens when toluene is—(*a*) nitrated, (*b*) sulphonated, (*c*) chlorinated, (*d*) treated with CH_3Cl in the presence of anhydrous $AlCl_3$, (*e*) treated with chromyl chloride, (*f*) oxidised with $KMnO_4$? (*Delhi B.Sc. Hons. Sub. 1976*)

6. Disuss what is meant by aromatic character.

7. (*a*) Explain the term aromaticity. What is meant by electrophilic substitution ? Illustrate your answer with reference to reactions of benzene.

(*b*) Give the mechanism of nitration. (*Delhi B.Sc. 1974*)

8. (*a*) How does benzene differ from aliphatic hydrocarbons ?

(*b*) Illustrate the differences between aromatic compounds and olefins by comparing reactions of benzene and ethylene with respect to the following reagents : (*i*) Hydrogen bromide ; (*ii*) Chlorine ; (*iii*) Concentrated sulphuric acid. With all reactions indicate the conditions required

9. (*a*) State Huckel's Rule. How can it be used to justify the aromatic nature of benzene, naphthalene and anthracene ?

(*b*) How are the relative positions of the methyl groups in different xylenes established ? (*Delhi B Sc.Hons. 1971*)

10. Define aromaticity and explain the stability of aromatic compounds in terms of the orbital picture and the Huckel's rule. Mention the typical reactions of such compounds and mechanism of any one of these reactions. (*Punjab B.Sc. 1974*)

11. (*a*) What is meant by Aromaticity ? State Huckel's rule and explain the stability of $\overset{+}{C_7H_7}$ cation and $C_5H_5^-$ anion

(*b*) Why is alkoxy group in benzene ring activating and ortho-para directing although oxygen is more electronegative than carbon ? (*G.N.D. B Sc. 1975*)

12 What are Arenes ? How will you prepare these by Friedel-Crafts alkylation, explain on the basis of reaction mechanism ? What are its limitations ? Explain the preference of Clemmensen or Wolff-Kishner reaction over Friedel-Crafts alkylation. (*Punjab B.Sc. 1975*)

13. Discuss the stability of benzene and its derivatives based on (*i*) Resonance, (*ii*) Heat of combustion, (*iii*) Heat of hydrogenation. (*G.N.D. B Sc. 1976*)

14. Explain the mechanism of Friedel-Crafts reaction (*Punjabi B.Sc. 1976*)

15. (*a*) Starting with $C_6H_5CH-CH_2$, how will you prepare the following :

(*i*) Ethylcyclohexane (*ii*) Benzoic acid
(*iii*) *p*-Chlorostyrene, and (*iv*) Polystyrene (*Punjab B.Sc. 1976*)

16. Describe the mechanisms of ring and side-chain halogenation of toluene, explaining clearly the conditions under which each reaction takes place.

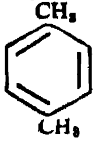
17. Discuss the mechanism of Friedel-Crafts alkylation and point out its limitations.

Short Answer Type :

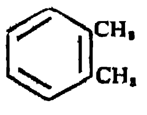
1. Indicate methods for obtaining benzene and trinitrotoluene from toluene (*Kerala B Sc. 1973*)

2 Predict the products formed when toluene is chlorinated (*Delhi B.Sc. Hons Sub. 1977*)

3. How can you differentiate between the following pairs of isomers ?



and



(*Delhi B.Sc. Hons 1977*)

4. Write equations for the following reactions :

(*i*) Sodium benzoate or sodium toluate+Soda lime (heat).

(*ii*) Phenol or *m*-Cresol+Zinc dust.

(*iii*) Benzenesulphonic acid or Toluenesulphonic acid+superheated steam or mineral acid (boil).

(*iv*) Benzenediazonium chloride or Toluenediazonium chloride+H_3PO_2.

(*v*) Acetophenone+Zn/Hg and conc HCl.

(*vi*) *n*-Hexane, *n*-Heptane or *n*-Octane+Cr_2O_3 at 770K.

5. What happens when benzene or toluene is treated with the following in the presence of anhydrous aluminium chloride ?

(*i*) methyl chloride,	(*ii*) formyl chloride,
(*iii*) acetyl chloride,	(*iv*) benzoyl chloride,
(*v*) carbonyl chloride,	(*vi*) chloroformamide,
(*vii*) methylene chloride,	(*viii*) chloroform,
(*ix*) ethylene,	(*x*) ethanol.

6. Complete the following reactions and write balanced equation for each

(*i*) Phenyl bromide+methyl iodide+metallic sodium→

(*ii*) *o*-Bromotoluene+methyl bromide+metallic sodium→

(*iii*) Phenylmagnesium bromide+methyl bromide→

(*iv*) Oxidation of (*i*) toluene, (*ii*) *o*-xylene, (*iii*) butylbenzene.

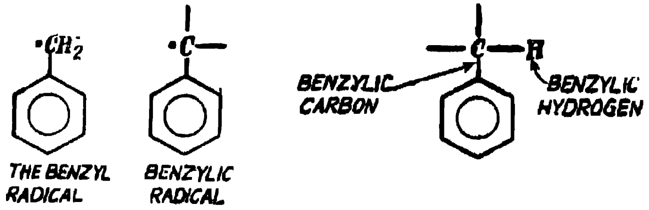
(*v*) Chlorination of benzene and toluene in cold, dark and presence of halogen carriers.

(*vi*) Chlorination of cold benzene and boiling toluene in light and absence of halogen carriers.

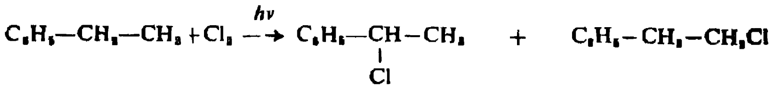
7. Does cyclotetraene exhibit aromatic character ? Give reasons for your answer.

8. Why does side-chain halogenation of an alkylbenzene occur preferentially at the benzylic hydrogen ? Explain at length.

[Hint. Benzylic radical is a general name for all radicals which have an unpaired electron on the side chain carbon directly attached to the benzene ring. This carbon atom is termed benzylic carbon and hydrogens attached to this carbon atom are called benzylic hydrogens.



9. Chlorination of ethylbenzene in presence of sunlight is represented as follows :



$$C_6H_5—CH_2—CH_3+Cl_2 \xrightarrow{h\nu} C_6H_5—\underset{\displaystyle Cl}{\underset{|}{C}H}—CH_3 \quad + \quad C_6H_5—CH_2—CH_2Cl$$

Ethylbenzene	1-chloro-1-phenylethane (91%)	2-chloro-1-phenylethane (9%)

(*a*) How can you justify the formation of 1-chloro-1-phenylethane as a major product ?

(*b*) What kind of free radical is involved in the formation of 2-chloro-1-phenylethane (a minor product) ?

(*c*) Name the major product you expect to be formed when *n*-propylbenzene is chlorinated in sunlight.

10. Write resonance structures of benzyl cation, $C_6H_5CH_2^+$.

11. Benzyl cation is more stable than a tertiary carbocation. Can you account for its exceptional stability ?

12. Would you expect that the positive charge of benzyl cation is delocalised ? If so, over which carbons ?

13. What does molecular orbital theory tell us about the location of the positive charge in benzyl cation ?

14. Knowledge of the substitution reactions of benzene nucleus and the reaction of side-chains of alkyl and alkenylbenzenes is helpful in the synthesis of a vast number of benzene derivatives. Planning a synthesis involves skilful decision about the order in which these reactions should be carried out.

How will you bring about the following conversions :

(*i*) Benzene into *p*-Bromonitrobenzene.

(*ii*) Toluene into *p*-nitrobenzoic acid.

(*iii*) Toluene into *m*-nitrobenzoic acid.

(*iv*) *n*-Propylbenzene into 1-(*p*-chlorophenyl)-propene.

(*v*) Acetanilide into *o*-nitroaniline.

15. Starting with benzene, toluene or aniline plan the synthesis of the following :

(*i*) *o*-Acetyltoluene

(*ii*) *o*-bromaniline

(*iii*) *o*-Toluic acid

(*iv*) *m*-Chlorobenzoic acid

(*v*) *p*-Bromoaniline

(*vi*) 2-Bromo-4-nitroaniline

(*vii*) *n*-Butylbenzene

(*viii*) 2-Bromo-4-nitrotoluene

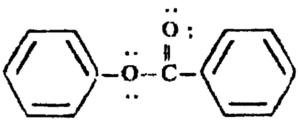
(*ix*) *p*-Bromobenzoic acid

(*x*) 4-Bromo-2-nitroaniline

(*xi*) 2, 4, 6-Trinitrotoluene

(*xii*) *m*-Nitrobenzylidene chloride.

16. Name the products you would expect from the nitration of phenyl benzoate,



17. Which ring of benzanilide is expected to undergo electrophilic substitution more readily ?

18. State Huckel's rule. Give any two examples to illustrate non-benzenoid aromatic compounds. (*Calicut B Sc. 1981* ; *Delhi 1981*)

19. Which of the following represents the principal nitrating species in the nitration of benzene with conc HNO_3 and conc H_2SO_4 :

NO_2^-, NO^+, NO_2^+, NO_3^- ?

Give the equation representing formation of the species.

(*Madurai Kamraj B.Sc. 1981*)

20 Toluene reacts with chlorine in the presence of sunlight and in the absence of halogen carrier to give benzyl chloride, benzoyl chloride or *o*-and *p*-chlorotoluenes. Select the correct product.

(*Madurai Kamaraj, B.Sc. 1981*)

Problems :

1. Identify the compounds **A, B, C, D** in the following :

(*a*) **A** is dichlorobenzene which may be prepared by the decarboxylation of three different acids with molecular formula $C_7H_4O_2Cl_2$.

(*b*) The dichlorobenzene **B** may be formed by the decarboxylation of only one acid with formula $C_7H_4O_2Cl_2$.

(*c*) The dihydroxybenzene **C** can give rise to only two mono-nitro derivatives.

(*d*) Xylene **D** gives only one mononitro derivative.

2. The compound **A** having the molecular formula C_8H_{10} gives on nitration with cold concentrated nitric acid two isomeric compounds **B** and **C** having molecular formula $C_8H_9NO_2$.

On oxidation **A** gives $C_8H_6O_4$ (**D**). **B** and **C** on oxidation give the isomers **E** and **F** respectively. Identify the compounds **A** to **F**.

3. On nuclear chlorination C_9H_{12} (**A**) gives only one product **B** which may be oxidised to $C_9H_5O_6Cl$ (**C**). **A** may also be chlorinated to give $C_9H_{11}Cl$, (D), $C_8H_6Cl_4$ (E) and $C_8H_4Cl_6$ (F). D, E and F on hydrolysis give halogen-free compounds G, H and I respectively. With CrO_2Cl_2 A gives C_8H_8O (J). Both A and J may be oxidised to $C_8H_6O_4$ which is identical with I.

Identify the various compounds A to J.

4. Two isomers A and B having molecular formula $C_9H_{12}O$ when distilled with zinc dust yield C_9H_{12} (C) which on oxidation with CrO_2Cl_2 gives $C_9H_{10}O$ (D) while with other oxidising agents it gives first $C_8H_8O_2$ (E) and then a *p*- compound $C_8H_6O_4$ (F). D may also be oxidised to F. Identify the compounds A to F.

5. Three isomeric hydrocarbons C_9H_{12} (A, B, C) oxidise to $C_9H_6O_6$ (D, E, F). While D may give three different mono-ethyl esters, E may form only two and F only one. Identify compounds A to F.

6. An organic compound A contains C=92·3% and H=7·7%. Its vapour density has been found to be 52. A is oxidised by $KMnO_4$ solution in cold and when fully oxidised gives an acid B which contains C=63·8% and H=4·9%. A reacts with bromine and yields a compound C containing 60·8% bromine. What is the structure of A ?

7. An organic compound A contains C=90·57% and H=9·43%. On oxidation it gave a crystalline dibasic acid B which gave the following results on analysis :

0·1826 g yielded 0·3872 g of CO_2 and 0·0594 g of H_2O. The silver salt of the acid contains 56·8% of silver. On heating the acid it is converted into compound C of the formula $C_8H_4O_3$. On distilling the acid B with lime, benzene is formed. Discuss the reactions and assign structural formulae to A, B, C and name them.

8. An aromatic hydrocarbon A containing C=91·3% and H=8·7% on treatment with chlorine gave three isomeric mono-chloro compounds X, Y, Z each having 28% chlorine. On oxidation with $KMnO_4$ all the three gave monobasic acids. The acid from X on distillation with soda lime gave benzene while those from Y and Z gave monochlorobenzene. What formulae would you assign to various compounds ?

ANSWERS

Short Answer Questions :

7. No, since it does not satisfy $4n+2$ rule with its 8π electrons.

8. Because benzylic radical is comparatively more stable due to resonance. The unpaired electron of the benzyl radical is delocalised over the benzylic carbon and the ortho and para carbons of the ring.

9. (*a*) It involves formation of a more stable benzylic radical as intermediate.

(*b*) Less stable primary free radical.

(*c*) 1-chloro-1-phenylpropane.

11. Due to resonance.

12. Over the benzylic carbon and the ortho and para carbons of the ring.

13. Same as resonance theory—see Ans. 12.

14. (*i*) By bromination followed by preparation of *o*- and *p*-derivatives by fractional distillation and then nitration of *p*-bromobenzene.

(*ii*) Nitration of toluene followed by separation of ortho- and para-nitrotoluenes. *p*-Nitrotoluene on oxidation gives *p*-nitrobenzoic acid.

(*iii*) Toluene on oxidation gives benzoic acid which on nitration gives *m*-nitrobenzoic acid.

(*iv*) First introduce Cl atom in the benzene ring by chlorination in cold

Next introduce the double bond in the benzene ring by benzylic chlorination followed by dehydrohalogenation.

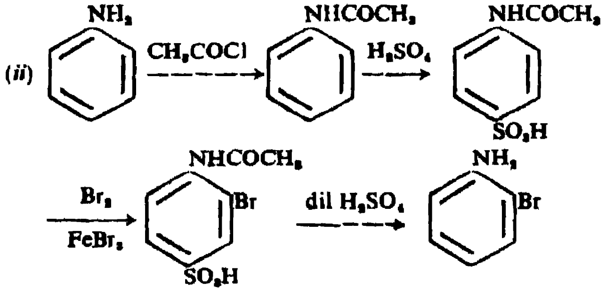
Is there any harm if we introduce double bond first and Cl atom next ?

(*v*) Sulphonation to introduce $-SO_3H$ group in para position followed by nitration and then desulphonation.

Here sulphonic group is serving only as a 'blocking group'.

15. (*i*) Toluene with $CH_3COCl + AlCl_3$ followed by separation of ortho and para-isomers

(*ii*)

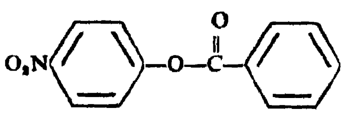


(*iii*) *o*-Acetyltoluene obtained in (*i*) above on oxidation with bromine solution in NaOH gives *o*-Toluic acid. (Br_2 + NaOH) oxidises $-COCH_3$ group to $-COOH$ group but does not affect CH_3 group.

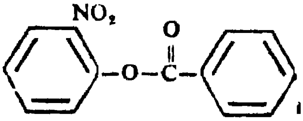
(*iv*) Toluene $\xrightarrow{[O]}$ Benzoic acid Cl_2, $FeCl_3$ ⟶ *m*-chlorobenzoic acid.

(*vi*) Toluene $\xrightarrow{HNO_3}$ *o* + *p*-nitrotoluene (isolate para isomer) $\xrightarrow{Br_2,\ FeBr_3}$ 2-Bromo-4-nitrotoluene.

16.



and



17. Benzene ring attached to $-\ddot{N}H-$ group.

Problems :

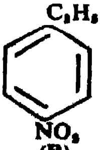
1. (*a*) A is *m*-Dichlorobenzene. (*b*) B is *p*-Dichlorobenzene.

(*c*) C is 1, 2-benzenediol (*o-dihydroxybenzene*). (*d*) D is *p*-xylene.

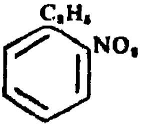
2. A is $C_6H_5C_2H_5$ (ethylbenzene). B is *p*-nitroethylbenzene.

C is *o*-nitroethylbenzene. D is benzoic acid, $C_6H_5.COOH$.

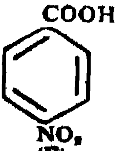
E is *p*-nitrobenzoic acid. F is *o*-nitrobenzoic acid



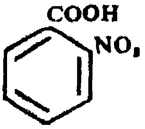
(B)



(C)

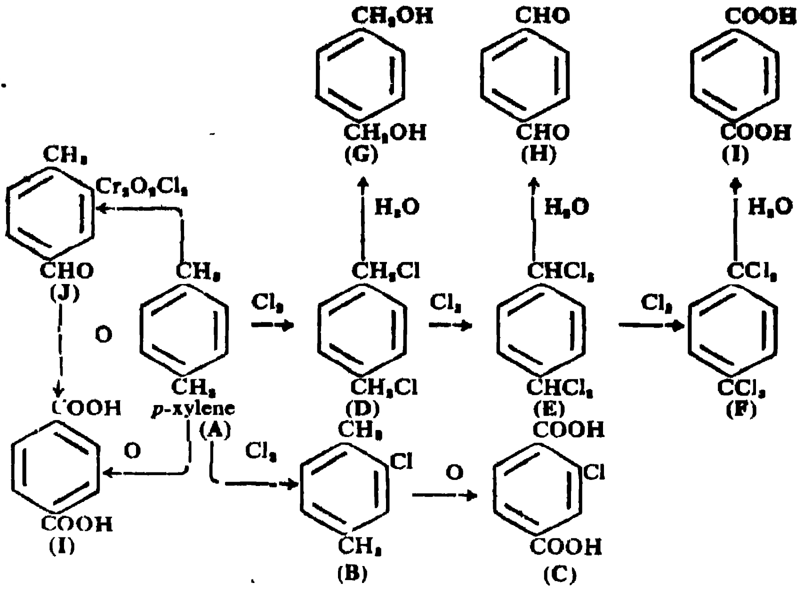


(E)

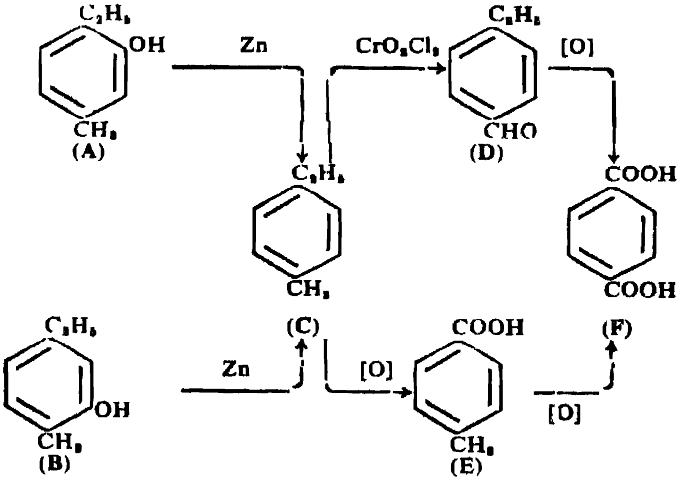


(F)

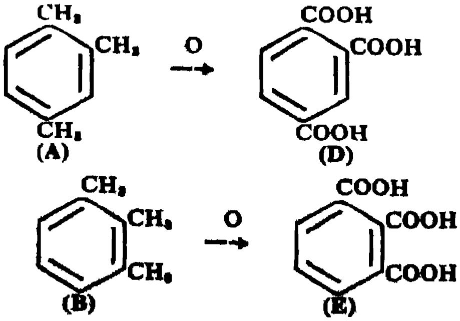
3.

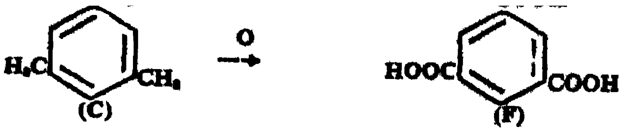

CH$_2$OH
CH$_2$OH
(G)
CHO
CHO
(H)
COOH
COOH
(I)
CH$_3$
Cr$_2$O$_2$Cl$_2$
CHO
(J)
O
COOH
COOH
(I)
H$_2$O
H$_2$O
H$_2$O
CH$_3$
CH$_3$
p-xylene
(A)
Cl$_2$
CH$_2$Cl
CH$_2$Cl
(D)
Cl$_2$
CHCl$_2$
CHCl$_2$
(E)
Cl$_2$
CCl$_3$
CCl$_3$
(F)
O
Cl$_2$
CH$_3$
Cl
CH$_3$
(B)
O
COOH
Cl
COOH
(C)

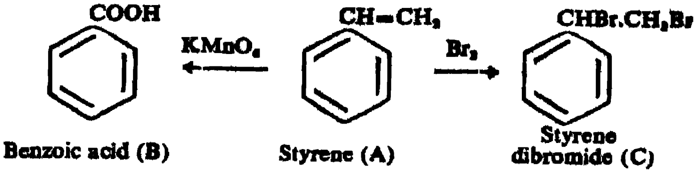
4.

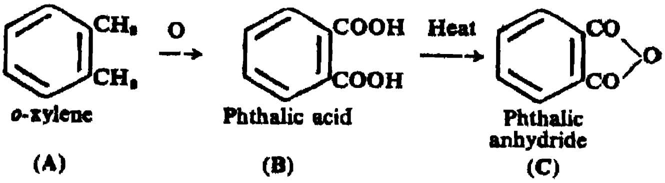

C$_2$H$_5$
OH
CH$_3$
(A)
Zn
CrO$_2$Cl$_2$
C$_2$H$_5$
CHO
(D)
[O]
C$_2$H$_5$
CH$_3$
(C)
COOH
COOH
(F)
C$_2$H$_5$
OH
CH$_3$
(B)
Zn
[O]
COOH
CH$_3$
(E)
[O]

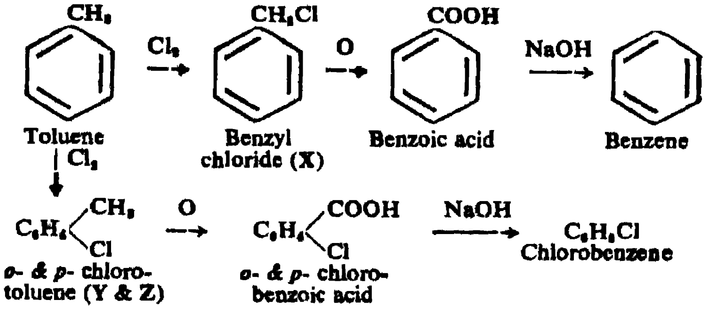
5.


CH$_3$
CH$_3$
CH$_3$
(A)
O
COOH
COOH
COOH
(D)
CH$_3$
CH$_3$
CH$_3$
(B)
O
COOH
COOH
COOH
(E)


H$_3$C
CH$_3$
(C)
O
HOOC
COOH
(F)

6. 
COOH
KMnO$_4$
CH=CH$_2$
Br$_2$
CHBr.CH$_2$Br
Benzoic acid (B)
Styrene (A)
Styrene dibromide (C)

7. 
CH$_3$
CH$_3$
O
COOH
COOH
Heat
CO
O
CO
o-xylene
(A)
Phthalic acid
(B)
Phthalic anhydride
(C)

8. 
CH$_3$
Cl$_2$
CH$_2$Cl
O
COOH
NaOH
Toluene
Benzyl chloride (X)
Benzoic acid
Benzene
Cl$_2$
C$_6$H$_4$
CH$_3$
Cl
O
C$_6$H$_4$
COOH
Cl
NaOH
C$_6$H$_5$Cl
Chlorobenzene
o- & p- chloro-toluene (Y & Z)
o- & p- chloro-benzoic acid

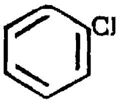
37

Aromatic Halogen Compounds

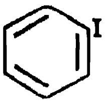
1. General.—There are three types of halogen compounds :

(*i*) **Addition Compounds**, *e.g.*, benzene hexahalides, $C_6H_6Cl_6$ and $C_6H_6Br_6$.

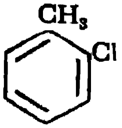
(*ii*) **Nuclear substitution products or Aryl halides.** These are halogen derivatives in which the halogen is linked directly to the carbon of the benzene nucleus, *e.g.*,



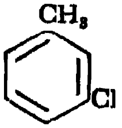
Chloro-benzene



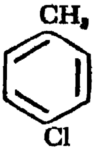
Iodo-benzene



o-chloro-toluene

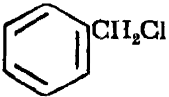


m-chloro-toluene

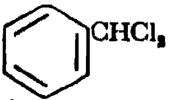


p-chloro-toluene

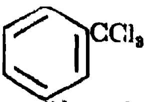
(*iii*) **Side-chain substitution products.** These are halogen derivatives in which halogen is linked to the carbon of the side-chain, *e.g.*,



Benzyl chloride



Benzylidene chloride



Benzylidyne chloride

2. General Methods of Preparation.—

(*a*) **Nuclear derivatives or Aryl halides.**

(*i*) **Direct halogenation.** *Low temperature and the presence of a halogen carrier favour nuclear substitution.* Chlorination and bromination are carried out in dark, at ordinary temperature in the presence of a catalyst (iron or aluminium amalgam). The amount of halogen determines the extent of halogenation.

For example, chlorination of benzene with one molecule of chlorine gives chlorobenzene whereas two molecules of chlorine yield a mixture of *o*- and *p*-dichlorobenzene, the latter predominating.

$$\underset{\text{Benzene}}{C_6H_6} + \underset{(\textit{one molecule})}{Cl_2} \xrightarrow{\text{Fe}} \underset{\text{Chlorobenzene}}{C_6H_5Cl} + HCl \quad (90\%)$$

$$C_6H_5Cl + \underset{\substack{(\textit{Second}\\ \textit{molecule})}}{Cl_2} \xrightarrow{\text{Fe}} \underset{\substack{\textit{o- \& p-}\text{dichloro-}\\ \text{benzene}}}{C_6H_4Cl_2} + HCl$$

Mechanism of Chlorination. The commonly accepted mechanism involves the following steps :

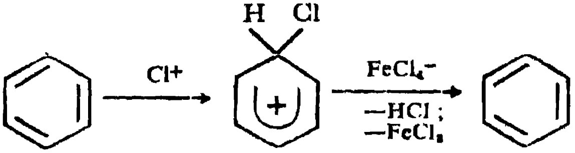
(*i*) $2Fe\ (catalyst) + 3Cl_2 \rightarrow 2FeCl_3$

(*ii*) $Cl_2 + FeCl_3 \rightarrow \overset{\delta+}{Cl}-\overset{\delta-}{Cl}-FeCl_3 \rightleftharpoons FeCl_4^- + Cl^+$

(*iii*) $Cl^+ + C_6H_6 \rightarrow \overset{+}{C_6H_6}\!<^{H}_{Cl}$

(*iv*) $\overset{+}{C_6H_6}\!<^{H}_{Cl} + FeCl_4^- \rightarrow C_6H_5Cl + HCl + FeCl_3$

or



Bromination of toluene in presence of iron (using one molecule of bromine) gives a mixture of *o*- and *p*-bromotoluenes.

$$C_6H_5CH_3 + Br_2 \xrightarrow{Fe} C_6H_4\!<^{CH_3}_{Br} + HBr$$

Toluene　　*o*- & *p*-bromotoluenes

Difficulty in preparing Iodo-derivatives. Iodo-derivatives cannot be prepared by direct iodination because the reaction is reversible and hydriodic acid produced is a strong reducing agent to reduce iodo-derivatives back to the hydrocarbon.

$$\underset{\text{Benzene}}{C_6H_6} + I_2 \rightleftharpoons \underset{\text{Iodo-benzene}}{C_6H_5I} + \underset{\text{Hydriodic acid}}{HI}$$

The difficulty is overcome by carrying on the reaction in presence of an oxidising agent, *e.g.*, iodic acid, nitric acid or mercuric oxide which oxidises the hydriodic acid to iodine, thus enabling the reaction to proceed forward.

$$5HI + HIO_3 \longrightarrow 3I_2 + 3H_2O$$

Thus iodobenzene can be obtained in good yield by iodination in presence of an oxidising agent.

$$2C_6H_6 + I_2 \xrightarrow[HNO_3]{[O]} 2C_6H_5I + H_2O \qquad (86\text{-}87\%)$$

(*ii*) **Action of phosphorus pentachloride on nuclear hydroxy compounds.** The hydroxyl group is replaced by chlorine atom, *e.g.*, phenol gives chlorobenzene but the yield is poor, the main product being triphenyl phosphate.

$$\underset{\text{Phenol}}{C_6H_5OH} + PCl_5 \longrightarrow \underset{\text{Chlorobenzene}}{C_6H_5Cl} + POCl_3 + HCl$$

(*iii*) **Sandmeyer's Reaction.** When a diazonium salt solution is run into a solution of cuprous halide dissolved in the corresponding halogen acid, the diazo-group is replaced by a halogen atom (For mechanism *see* page *2·456*). For example,

$$\underset{\text{Benzenediazonium chloride}}{C_6H_5N_2^+Cl^-} \xrightarrow{CuCl/HCl} \underset{\text{Chlorobenzene}}{C_6H_5Cl} + N_2$$

$$C_6H_5.N_2^+Cl^- \xrightarrow{CuBr/HBr} \underset{\text{Bromobenzene}}{C_6H_5Br} + N_2$$

$$ArN_2^+X^- \xrightarrow[-HX]{HBF_4} \underset{\text{Diazonium fluoborate}}{ArN_2^+BF_4^-} \xrightarrow{\text{heat}} ArF + BF_3 + N_2$$

Iodo-compounds may be obtained by boiling the diazonium salt solution with aqueous potassium iodide.

$$C_6H_5.N{=}NCl + KI \longrightarrow C_6H_5I + KCl + N_2 \quad (74\text{-}76\%)$$

This is the most satisfactory method for preparing nuclear halogen derivatives.

(*iv*) **Action of bromine on silver salts of aromatic acids.**

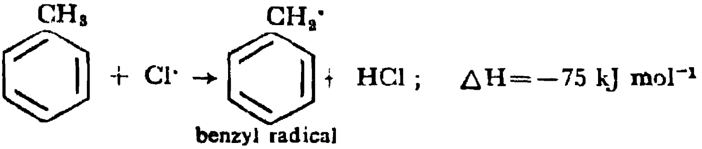
$$C_6H_5COOAg + Br_2 \longrightarrow C_6H_5Br + CO_2 + AgBr \quad (53\%)$$

(*b*) **Side-chain Derivatives.**

(*i*) **Direct halogenation.** *High temperature, light and absence of halogen carriers favour side-chain substitution, e.g.*, chlorination of toluene at its boiling point and in the presence of light.

$$\underset{\text{Toluene}}{C_6H_5CH_3} \xrightarrow[-HCl]{Cl_2} \underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} \xrightarrow[-HCl]{Cl_2} \underset{\text{Benzylidene chloride}}{C_6H_5CHCl_2} \xrightarrow[-HCl]{Cl_2} \underset{\text{Benzylidyne trichloride}}{C_6H_5CCl_3}$$

Side-chain halogenation proceeds *via* free radical mechanism. This is because of the low bond dissociation energy of the benzyl-hydrogen bond.



Like allyl radical benzyl radical is stabilized by delocalization of odd electron into the ring which diffuses the free radical character of the molecule. This conjugation can be represented by orbital overlap between $2p$ orbital of benzylic carbon atom containing odd electron and the π system of the benzene ring (Fig. 37·1).

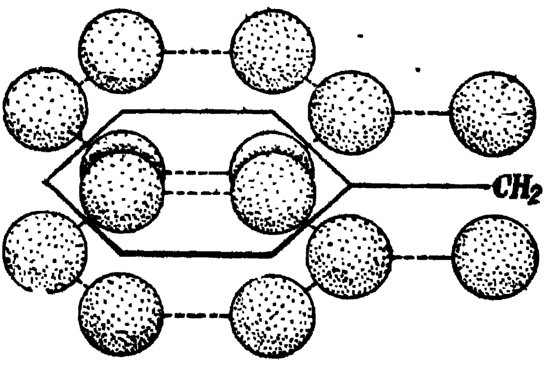
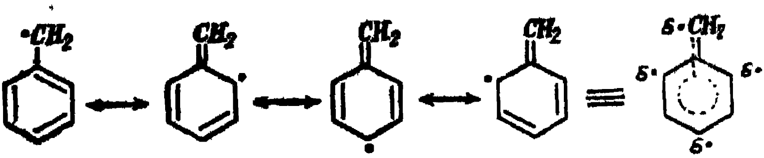


Fig. 37·1—Delocalization of benzyl radical.

Alternatively, the conjugated system can be visualised resonance hybrid of the following structures.

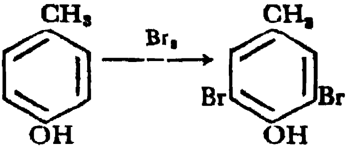


The unpaired electron is delocalized over the benzylic carbon and the ortho and para carbons of the ring.

In the next step benzyl radical reacts with chlorine to regenerate a chlorine atom which then continues the chain.

$$C_6H_5CH_2^{\cdot} + Cl_2 \rightarrow C_6H_5CH_2Cl + Cl^{\cdot}$$

When an activating group OH or NH_2 is present in the ring, side-chain halogenation is extremely difficult, if not impossible. For example, 4-methylphenol on bromination yields 2, 6-dibromo-4-methylphenol



4-Methylphenol 2, 6-dibromo-4-methylphenol

When the side-chain is larger than a methyl group, its halogenation is more complicated, *e.g.*, chlorination of ethylbenzene at its boiling point and in presence of light first gives a mixture of α- and β-chloroethylbenzene and finally pentachloroethylbenzene is produced.

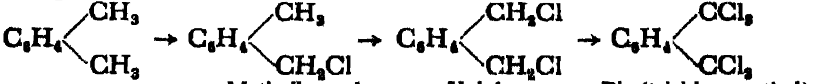
$$C_6H_5CH_2.CH_3 \xrightarrow{Cl_2} \underset{\alpha\text{-isomer}}{C_6H_5.CHCl.CH_3} + \underset{\beta\text{-isomer}}{C_6H_5CH_2.CH_2Cl}$$

$$\xrightarrow{Cl_2} \underset{\text{Pentachloroethylbenzene}}{C_6H_5CCl_2.CCl_3}$$

Chlorination in cold and in presence of light gives α-isomer as the main product.

$$C_6H_5CH_2CH_3 \xrightarrow{Cl_2} C_6H_5CHCl.CH_3 \xrightarrow{Cl_2} C_6H_5CCl_2.CH_3$$

In case two side-chains are present as in xylene both may be halogenated.



$$C_6H_4\begin{matrix}\diagup CH_3\\ \diagdown CH_3\end{matrix} \rightarrow C_6H_4\begin{matrix}\diagup CH_3\\ \diagdown CH_2Cl\end{matrix} \rightarrow C_6H_4\begin{matrix}\diagup CH_2Cl\\ \diagdown CH_2Cl\end{matrix} \rightarrow C_6H_4\begin{matrix}\diagup CCl_3\\ \diagdown CCl_3\end{matrix}$$

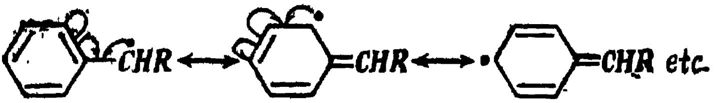
Methylbenzyl chloride Xylylene chloride Bis-(trichloromethyl) benzene

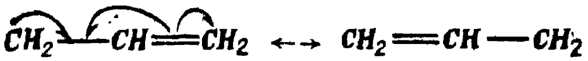
It is rather curious that o-xylene is not fully chlorinated while *m*- and *p*-xylenes give fully chlorinated products. The reason may be spatial effect in the case of *o*-xylene.

Use of N-Bromosuccinimide (NBS). Allylic and benzylic positions undergo free radical bromination readily with NBS. It is believed that NBS furnishes a low concentration of Br_2 which itself effects the actual radical bromination. (See page *2·33*).

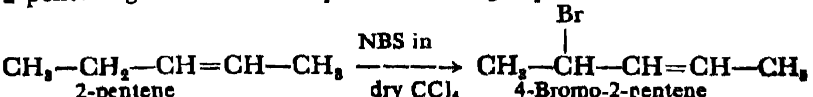
However, in the presence of traces of water or with polar substrates which undergo rapid electrophilic substitution, NBS brings about nuclear bromination. For example, phenol when treated with NBS gives *p*-bromophenol.

The particularly ready attack on benzylic or allylic position is due to stabilisation of the first formed radical by delocalisation.





Generally NBS brings about bromination of allylic *methylene* group more readily than that of allylic *methyl* groups. For example, 2-pentene gives 4-bromo-2-pentene as major product.



$$\underset{\text{2-pentene}}{CH_3{-}CH_2{-}CH{=}CH{-}CH_3} \xrightarrow[\text{dry } CCl_4]{\text{NBS in}} \underset{\substack{\text{4-Bromo-2-pentene}\\ \text{(major product)}}}{CH_3{-}\overset{\overset{\displaystyle Br}{|}}{C}H{-}CH{=}CH{-}CH_3}$$

(*ii*) **By the action of phosphorus pentachloride on aromatic alcohols and aldehydes,** *e.g.*, on benzyl alcohol and benzaldehyde.

$$\underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + PCl_5 \longrightarrow \underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} + POCl_3 + HCl$$

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + PCl_5 \longrightarrow \underset{\text{Benzylidene chloride}}{C_6H_5CHCl_2} + POCl_3$$

3. General Physical Properties of Halogen Derivatives.

(*i*) Halogen derivatives are colourless liquids or crystalline solids, insoluble in water but soluble in organic solvents.

Their boiling points and densities are greater than those of the parent arenes.

(*ii*) These are all heavier than water. The boiling points and densities of monohalogen derivatives of benzene (which are all liquids) are in the order :

Iodo > Bromo > Chloro

(*iii*) The side-chain derivatives possess an irritating smell while the nuclear compounds have an agreeable odour.

4. Chemical Properties of Nuclear Derivatives (Aryl halides).

(*a*) **Reaction of the Halogen Atom.** *In the case of nuclear halogen derivatives, the halogen atom is firmly attached to the nucleus and is not easily displaced by* OH, NH_2, CN, *etc*. The nuclear derivatives thus differ very much from the alkyl halides.

Under special conditions, however, the halogen atom attached to the nucleus may be replaced.

(1) **Nucleophilic aromatic substitution.**

$$Ar:X + :Z^- \rightarrow Ar:Z + :X^-$$

(*i*) *Replacement by Hydroxyl Group.* The halogen atom is replaced by hydroxyl when an aryl halide is heated with 10 per cent aqueous sodium hydroxide or sodium carbonate under pressure (200 atm) at about 570K in the presence of copper salt (*catalyst*).

$$\underset{\text{Phenyl chloride}}{C_6H_5Cl} + NaOH \xrightarrow[\text{200 atm}]{\text{570K}} \underset{\text{Phenol}}{C_6H_5OH} + NaCl$$

(*ii*) *Replacement by Amino group.* The halogen atom is replaced by an amino group when the aryl halide is heated with aqueous ammonia in the presence of cuprous oxide at 470K under pressure.

$$2C_6H_5Cl+2NH_3+Cu_2O \longrightarrow 2C_6H_5NH_2+2CuCl+H_2O \quad (90\%)$$

(*iii*) *Replacement by Cyanide group.* In an aryl bromide bromine atom is replaced by a cyanide group when heated with KCN and cuprous cyanide in the presence of pyridine or dimethylformamide (DMF) at 470K *e.g.*,

$$\underset{\text{Phenyl bromide}}{C_6H_5Br} \xrightarrow[\text{in DMF}]{\text{KCN, CuCN}} \underset{\text{Phenyl cyanide}}{C_6H_5CN} + CuBr$$

Mechanism of Nucleophilic Aromatic Substitution. The replacement of a hydrogen atom or a substituent attached to benzene nucleus by a nucleophile is termed nucleophilic aromatic substitution. This proceeds in general by three types of mechanism :

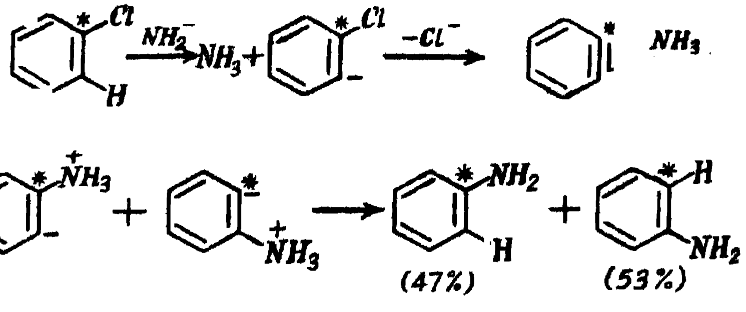
(*i*) **Unimolecular mechanism.** (see page 2·456)

(*ii*) **Bimolecular mechanism.** (see page 2·456). It proceeds *via* an intermediate σ-complex, the benzenonium carbanion or the cyclohexa-dienyl carbanion, *e.g.*,

The energy profile diagram is similar to the one given for electrophilic substitution on page 2·455.

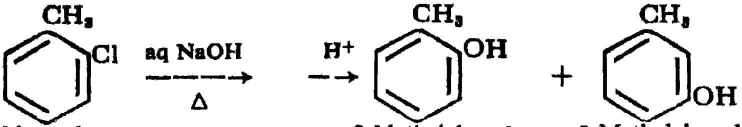
(*iii*) **Elimination-addition mechanism.** According to this mechanism it is accepted that nucleophilic aromatic substitution involves two steps : (*a*) Formation of benzyne by a *stepwise* elimination, followed by (*b*) stepwise addition to benzyne to form the products.

For example, when chlorobenzene with carbon atom of the C--Cl group labelled with ^{14}C is treated with potassium in liquid ammonia, aniline is obtained as follows :



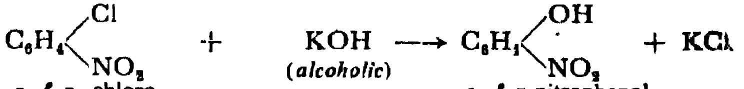
We find that the amino-group enters partly at the labelled carbon atom and partly at the *ortho*-carbon atom.

This proves that conversion of chlorobenzene into aniline is not a simple displacement as it appears to be. It proceeds *via* the elimination-addition mechanism involving the formation of benzyne as an intermediate product. *o*-Chlorotoluene on heating with aq NaOH gives a mixture of 2- and 3-methylphenol.



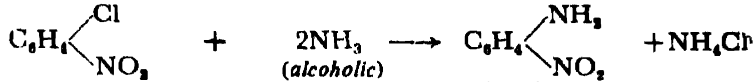
o-chlorotoluene 2-Methylphenol 3-Methylphenol

(*iv*) *Activation of Halogen atom.* An electron-withdrawing group, *e.g.*, nitro, cyano or carboxyl group when present in the *ortho*- or *para*- position to the halogen atom, makes it labile and replaceable by other groups. For example, *o*- and *p*-chloronitrobenzenes give corresponding nitrophenols and nitroanilines when treated at about 430-470K with alcoholic potash and alcoholic ammonia respectively.



$$C_6H_4\left<\begin{matrix}Cl\\NO_2\end{matrix}\right. + \underset{(alcoholic)}{KOH} \longrightarrow C_6H_4\left<\begin{matrix}OH\\NO_2\end{matrix}\right. + KCl$$

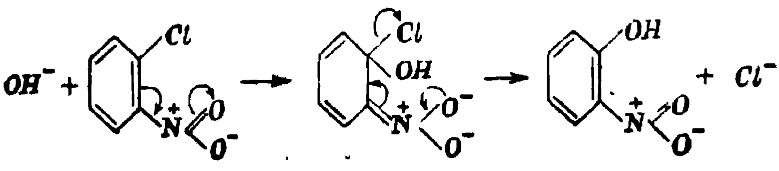
o- & *p*- chloronitrobenzene *o*- & *p*-nitrophenol



$$C_6H_4\left<\begin{matrix}Cl\\NO_2\end{matrix}\right. + \underset{(alcoholic)}{2NH_3} \longrightarrow C_6H_4\left<\begin{matrix}NH_2\\NO_2\end{matrix}\right. + NH_4Cl$$

o- & *p*-nitroaniline

Mechanism of the Reaction. These are examples of activated nucleophilic aromatic substitution wherein the activation of the halogen atom is believed to be due to the electron-withdrawing (−I) effect of the nitro- or carboxyl group



Thus in nucleophilic aromatic substitution reaction of aryl halides the presence of electron-withdrawing groups (*e.g.*, $-NO_2$, $-CN$, $-SO_3H$, $-COOH$ $-CHO$, $-COR$, $-\overset{+}{N}(CH_3)_3$, $-N_2^+$) activates the halogen atom. However, the nitro group and diazo group ($-N_2^+$) are by far the most powerful activators. On the other hand, presence of electron-releasing groups (*e.g.*, $-NH_2$, $-OH$, $-OR$, $-R$) deactivates the halogen atom.

(2) **Reduction.** An aryl halide, on reduction with a nickel-aluminium alloy in the presence of alkali, yields the parent hydrocarbon.

$$\underset{\text{Chlorobenzene}}{C_6H_5Cl} + 2[H] \xrightarrow[NaOH]{Ni/Al} \underset{\text{Benzene}}{C_6H_6} + HCl$$

(3) **Formation of Grignard Reagents.** Aryl bromides and aryl iodides but not aryl chlorides form Grignard reagents when treated with dry magnesium powder in dry ether.

$$\underset{\text{Phenyl bromide}}{C_6H_5Br} + Mg \xrightarrow{\text{Dry ether}} \underset{\text{Phenylmagnesium bromide (Grignard reagent)}}{C_6H_5Mg.Br}$$

The aryl chlorides, however, form Grignard reagents in tetrahydrofuran or in the presence of some methyl iodide (termed *entrainment method*).

(4) **Wurtz-Fittig or Fittig Reaction.** This is carried out by the action of an ethereal solution of an aryl halide with an alkyl halide in presence of sodium.

$$\underset{\text{Bromobenzene}}{C_6H_5Br} + \underset{\text{Ethyl bromide}}{C_2H_5Br} + 2Na \longrightarrow \underset{\text{Ethylbenzene}}{C_6H_5.C_2H_5} + 2NaBr \ (60\%)$$

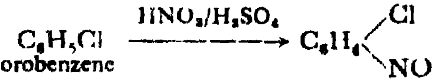
The reaction which involves the use of both alkyl and aryl halides is called Wurtz-Fittig reaction or Fittig reaction (*cf.*, Wurtz reaction which involves the use of alkyl halide only).

(5) **Ullmann Synthesis** (1903). When iodobenzene is heated with copper powder in a sealed tube, diphenyl is obtained.

$$2C_6H_5I + 2Cu \longrightarrow C_6H_5.C_6H_5 + 2CuI$$

Aryl chlorides and bromides do not react unless there is some negative group *o*- or *p*- to the halogen atom.

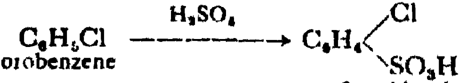
(*b*) **Reactions of the Benzene Nucleus.** The aryl halides can be nitrated, sulphonated and further halogenated when the nuclear hydrogen atom in *ortho*- and *para*- positions to the halogen atom is substituted, *i.e.*,



$$C_6H_5Cl \xrightarrow{HNO_3/H_2SO_4} C_6H_4\begin{cases}Cl\\NO_2\end{cases}$$

Chlorobenzene

o- & *p*-nitrochlorobenzene



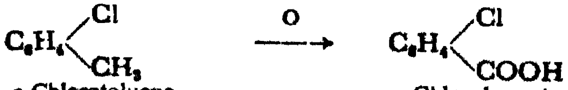
$$C_6H_5Cl \xrightarrow{H_2SO_4} C_6H_4\begin{cases}Cl\\SO_3H\end{cases}$$

Chlorobenzene

o- & *p*-chlorobenzene-sulphonic acid

$$\underset{\text{Chlorobenzene}}{C_6H_5Cl} \xrightarrow{Cl_2} \underset{o\text{- \& }p\text{-dichlorobenzene}}{C_6H_4Cl_2}$$

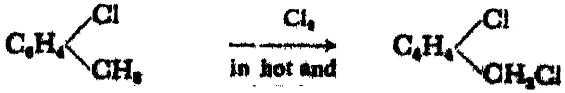
(*c*) **Reaction of the side-chain.** (*i*) On oxidation side-chain, if any, is oxidised to a carboxyl group. For example,



$$C_6H_4\begin{cases}Cl\\CH_3\end{cases} \xrightarrow{O} C_6H_4\begin{cases}Cl\\COOH\end{cases}$$

o-Chlorotoluene *o*-Chlorobenzoic acid

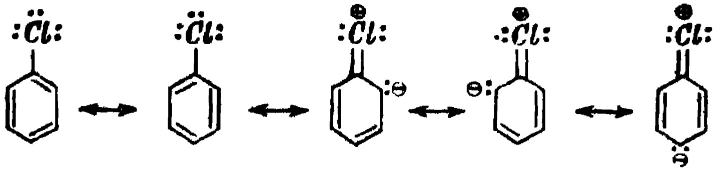
(*ii*) On halogenation in hot and in presence of light, substitution takes place in the side-chain.



$$C_6H_4\begin{cases}Cl\\CH_3\end{cases} \xrightarrow[\text{in hot and}]{Cl_2} C_6H_4\begin{cases}Cl\\CH_2Cl\end{cases}$$

5. Low Reactivity of Aryl Halides.—Low reactivity of aryl halides has been attributed to two different factors : (*i*) *delocalization of electrons by resonance* ; and (*ii*) *bond energies due to differences in hybridization.*

(*a*) *Resonance interpretation.* Chlorobenzene considered to be a hybrid of structures I to V, in which chlorine is joined to carbon



I II III IV V

by a double bond and carries a positive charge (see III, IV and V), whereas the ortho and para positions of ring bear a negative charge. Resonance stabilizes chlorobenzene and the double bond character of the carbon-chlorine bond makes it stronger than if it were a pure single bond.

Reactions of S_N2 or S_N1 type characteristic of alkyl halides do not take place with aryl halides because the halogen lies in the plane of the ring, a nucleophile cannot approach from the back side, and S_N2 mechanism cannot operate. Because of resonance with nucleus, halogen has little tendency to ionize and permit S_N1 mechanism. Hence simple aryl halides do not react with nucleophiles such as hydroxide, alkoxide, [illegible] or cyanide ion or with ammonia under conditions that bring about displacement reaction with alkyl halides.

(*b*) *Bond energies interpretation.* In alkyl halides the carbon holding halogen is sp^3 hybridized. In aryl halides, carbon is sp^2 hybridized ; the carbon-halogen bond is shorter and stronger and the molecule is more stable. C—Cl bond length in chlorobenzene has been actually found to be 1·69Å as compared with the length of 1·77-1·80Å in a large number of alkyl chlorides.

6. Chemical Properties of Side-chain Derivatives (Aralkyl halides).—As will be seen from the reactions given below, side-chain halogen derivatives behave like alkyl halides in most respects. Therefore, these should better be regarded as aryl-substituted alkyl halides and not as aryl halides.

(*a*) **Reactions of the Halogen atom.**

(1) **Replacement Reactions.** The side-chain halogen derivatives are very active like halides. The halogen atom is easily replaced by groups like —NH_2, —OH, —CN, —NO_2 etc.

$$C_6H_5CH_2\boxed{Cl + K}OH \rightarrow C_6H_5CH_2OH + KCl$$

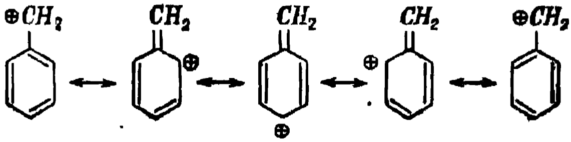
Benzyl chloride (*aqueous*) **Benzyl alcohol**

$$C_6H_5CH_2\boxed{Cl + H}NH_2 \rightarrow C_6H_5CH_2NH_2 + HCl$$

Benzyl chloride (*alcoholic*) **Benzylamine**

$$C_6H_5CH_2\boxed{Cl + K}CN \rightarrow C_6H_5CH_2CN + KCl$$

Benzyl chloride like alkyl chloride is highly reactive. The benzyl cation is stabilized by resonance, hence ionization mechanism is applicable to these reactions.



Contributing structures of the benzyl cation.

(2) **Friedel-Crafts Reactions.** Side-chain halogen derivatives react with aromatic hydrocarbons in presence of anhydrous aluminium chloride to give their higher homologues (*cf.*, alkyl halides). Nuclear halogen derivatives do not give this reaction.

$$C_6H_5\boxed{H + Cl}CH_2.C_6H_5 \rightarrow C_6H_5.CH_2C_6H_5 + HCl$$

Benzene Benzyl chloride Diphenylmethane

(3) **Fittig or Wurtz-Fittig Reaction.** Just like aryl halides, side-chain halogen derivatives react with alkyl or aryl halides and metallic sodium in dry ether.

$$C_6H_5CH_2\boxed{Cl + 2Na + Cl}CH_3 \rightarrow C_6H_5CH_2CH_3 + 2NaCl$$

Benzyl chloride Methyl chloride Ethylbenzene

$$C_6H_5\boxed{Cl + 2Na + Cl}CH_2C_6H_5 \rightarrow C_6H_5CH_2C_6H_5 + 2NaCl$$

Chlorobenzene Benzyl chloride Diphenylmethane

(4) **Formation of Grignard Reagents.** Side-chain halogen derivatives resemble aryl halides in forming Grignard reagents when these are heated with dry magnesium powder in dry ether.

$$C_6H_5CH_2Br + Mg \longrightarrow C_6H_5.CH_2.MgBr$$

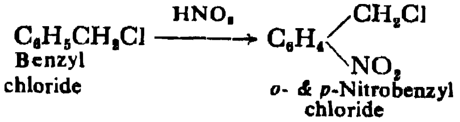
Benzyl bromide Benzylmagnesium bromide

(5) **Reduction.** Side-chain halogen derivatives on reduction with nascent hydrogen yield the parent hydrocarbon.

$$C_6H_5CH_2Cl + 2[H] \longrightarrow C_6H_5.CH_3 + HCl$$

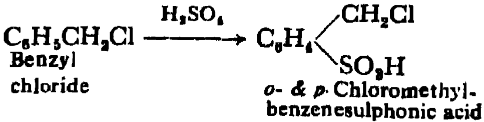
Benzyl chloride Toluene

(*b*) **Reactions of the Benzene Nucleus.** Both nuclear and the side-chain halogen derivatives possess a benzene nucleus and give usual electrophilic substitution reactions, *e.g.*, nitration, sulphonation, and halogenation. The newly-entering group enters the *ortho* and *para*- positions.



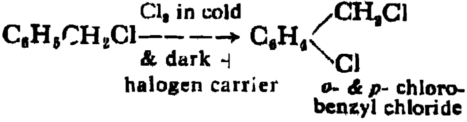
$$C_6H_5CH_2Cl \xrightarrow{HNO_3} C_6H_4\begin{cases}CH_2Cl\\ NO_2\end{cases}$$

Benzyl chloride *o*- & *p*-Nitrobenzyl chloride



$$C_6H_5CH_2Cl \xrightarrow{H_2SO_4} C_6H_4\begin{cases}CH_2Cl\\ SO_3H\end{cases}$$

Benzyl chloride *o*- & *p*-Chloromethylbenzenesulphonic acid

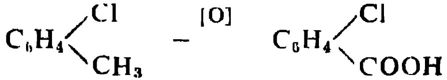


$$C_6H_5CH_2Cl \xrightarrow[\text{\& dark + halogen carrier}]{Cl_2 \text{ in cold}} C_6H_4\begin{cases}CH_2Cl\\ Cl\end{cases}$$

o- & *p*- chlorobenzyl chloride

(c) Reactions of the side-chain.

(i) Oxidation. On oxidation the side-chain along with the halogen atom is oxidised to a carboxyl group. This reaction is employed to know whether the halogen atom is present in the nucleus or the side-chain. If the halogen atom is lost during oxidation, it was present in the side-chain and in case it is not lost during oxidation it was attached to the nucleus.



$$C_6H_4\begin{smallmatrix}Cl\\CH_3\end{smallmatrix} \xrightarrow{[O]} C_6H_4\begin{smallmatrix}Cl\\COOH\end{smallmatrix}$$

o-chlorotoluene (*Cl attached to nucleus*) — *o*-chlorobenzoic acid (*Cl not lost during oxidation*)

$$C_6H_5CH_2Cl \xrightarrow{[O]} C_6H_5COOH$$

Benzyl chloride (*Cl present in side-chain*) — Benzoic acid (*Cl lost during oxidation*)

(ii) **Halogenation.** On halogenation in sunlight or ultraviolet rays more hydrogen atoms of the side-chain are replaced by halogen atoms. For example,

$$C_6H_5CH_2Cl \xrightarrow{Cl_2} C_6H_5CHCl_2 \xrightarrow{Cl_2} C_6H_5CCl_3$$

Benzyl chloride — Benzylidene chloride — Benzylidyne chloride

7. Comparative study of Nuclear and Side-chain derivatives

Points of Difference

Nuclear Derivatives	**Side-chain Derivatives**
1. Agreeable odour.	1. Irritating smell and lachrymatory (bring tears into the eyes)
2. Halogen atom firmly attached, not easily replaced by OH, NH_2, CN, etc.	2. Halogen atom very reactive ; easily replaced by these groups.
3. Do not give Friedel-Crafts reaction with benzene or toluene	3. Give Friedel Crafts reaction with benzene or toluene
4. Halogen atom not affected by oxidation.	4. The whole side-chain gives carboxyl group—the halogen atom is thus knocked off

Points of Resemblance

1. Both types of halogen derivatives give Wurtz Fittig and Fittig reaction.

2. Both react with dry magnesium powder in dry ether or tetrahydrofuran to form Grignard reagents

3. Both nuclear and side-chain derivatives give the reactions of the benzene nucleus, *e g.*, nitration, sulphonation, further halogenation. The new substituent enters the *ortho-* and *para*-positions

4. Both types give parent hydrocarbons when reduced with nascent hydrogen.

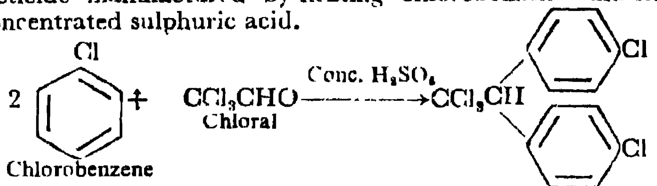
INDIVIDUAL MEMBERS

8. Chlorobenzene (Phenyl chloride), C_6H_5Cl.—It can be prepared by any of the general methods given before but it is produced commercially by passing a mixture of benzene vapour, air and hydrogen chloride over a catalyst (copper chloride)—*Raschig process.*

$$2C_6H_6 + 2HCl + O_2 \xrightarrow{CuCl_2} 2C_6H_5Cl + 2H_2O$$

Chlorobenzene is a colourless, pleasant-smelling heavy liquid (b.p. 405K ; Sp. Gr. 1·28) insoluble in water but soluble in alcohol and ether. It is a typical nuclear halogen derivative and its properties are given under 'general reactions'.

It is used for the manufacture of phenol, aniline and DDT—an insecticide manufactured by heating chlorobenzene and chloral with concentrated sulphuric acid.



p, p'- dichlorodiphenyltrichloroethane (DDT)
[2, 2 - bis (*p*-chlorophenyl)-1, 1, 1 -trichloroethane]

9. Bromobenzene (Phenyl bromide), C_6H_5Br.—Bromobenzene can be prepared by any of the general methods (page 2·507) but is obtained in the laboratory by bromination of benzene in the presence of a little iron powder (*halogen carrier*).

It is a colourless, heavy liquid (b.p. 428K ; Sp. Gr. 1·49) and closely resembles chlorobenzene.

10. Iodobenzene (Phenyl iodide), C_6H_5I.—It may be prepared in the laboratory by heating benzene and iodine with an oxidising agent (nitric or iodic acid) in a sealed tube, or by warming an aqueous solution of benzenediazonium chloride with potassium iodide.

$$2C_6H_6 + I_2 + [O] \xrightarrow{HIO_3} 2C_6H_5I + H_2O$$

$$\underset{\text{Benzenediazonium chloride}}{C_6N_5N:NCl} + KI \longrightarrow \underset{\text{Iodobenzene}}{C_6H_5I} + N_2 + KCl$$

It is a colourless, heavy liquid (b.p. 461K ; Sp. Gr. 1·861) and is more reactive than phenyl chloride or bromide. Iodobenzene reacts with chlorine to form iodobenzene dichloride which gives iodosobenzene, when treated with NaOH solution. Iodosobenzene on boiling with water gives iodoxybenzene.

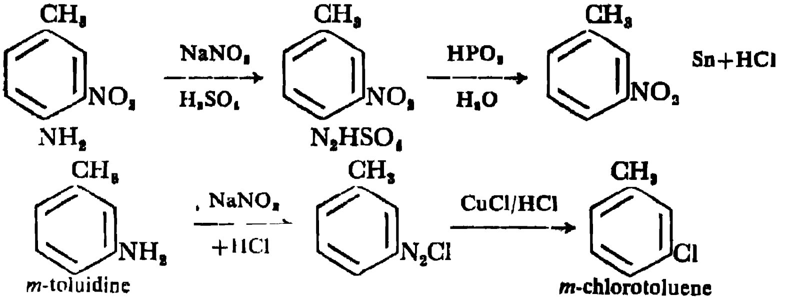
$$C_6H_5I \xrightarrow{Cl_2} \underset{\text{Iodobenzene dichloride}}{C_6H_5ICl_2} \xrightarrow{NaOH} \underset{\text{Iodosobenzene}}{C_6H_5IO}$$

$$\underset{\text{Iodosobenzene}}{2C_6H_5IO} \xrightarrow[\text{with water}]{\text{Boil}} \underset{\text{Iodoxybenzene}}{C_6H_5IO_2} + C_6H_5I$$

Both iodosobenzene and iodoxybenzene explode without melting when heated.

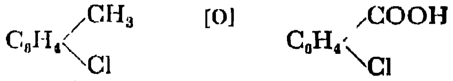
11. Chlorotoluenes (Tolyl chlorides), $CH_3.C_6H_4Cl$.—Three isomeric chlorotoluenes (*o-*, *m-* & *p-*) are known. The ortho- and para-chlorotoluenes are prepared by direct chlorination of cold toluene in presence of a halogen carrier. The meta- derivatives, which cannot be prepared by direct chlorination, are prepared by an indirect method.

On nitration of *p*-toluidine after protecting the amino group we get 3-nitro-4-aminotoluene. This on diazotisation followed by reduction gives *m*-nitrotoluene. The yield is 62-72%. *m*-Nitrotoluene on reduction gives *m*-toluidine which on diazotisation followed by Sandmeyer's reaction yields *m*-chlorotoluene.



m-toluidine *m*-chlorotoluene

These are colourless, pleasant-smelling, heavy liquids, immiscible with water. They resemble chlorobenzene in chemical properties and on oxidation give the corresponding chlorobenzoic acids.



$$C_6H_4{<}\begin{matrix}CH_3\\ Cl\end{matrix} \qquad [O] \qquad C_6H_4{<}\begin{matrix}COOH\\ Cl\end{matrix}$$

o-, *m*-, & *p*- Chlorotoluenes *o*- *m*- & *p*- Chlorobenzoic acid

12. Benzyl chloride (Phenylmethyl chloride), $C_6H_5CH_2Cl$ —Benzyl chloride is industrially prepared by passing chlorine through boiling toluene until the theoretical increase in weight is obtained.

$$\underset{\text{Toluene}}{C_6H_5CH_3}+Cl_2 \longrightarrow \underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} + HCl \qquad (60\%)$$

It may also be prepared by heating benzene with formalin and hydrochloric acid in presence of anhydrous $ZnCl_2$ (*Chloromethylation of Benzene*).

$$C_6H_6 + \underset{\text{Formalin}}{HCHO} + HCl \xrightarrow[-H_2O]{ZnCl_2} \underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl}$$

Mechanism suggested for chloromethylation is :

$$CH_2O+H^+ \rightleftharpoons CH_2OH \xrightarrow{ArH} ArCH_2OH+H^+ \quad \overset{HCl}{} \quad ArCH_2Cl+H_2O$$

The mechanism suggested above is supported by the fact that electron-releasing groups facilitate the reaction whereas electron-withdrawing groups retard the reaction.

It is a colourless liquid (b.p. 452K) with an irritating smell. It is immiscible with water but soluble in alcohol and ether. Chemically, it behaves like an alkyl halide. Actually the chlorine atom in benzyl chloride is more reactive than in methyl chloride. Thus when heated with aqueous potash, aqueous potassium cyanide or alcoholic ammonia, benzyl chloride gives benzyl alcohol, $C_6H_5CH_2OH$, benzyl cyanide, $C_6H_5CH_2CN$ and benzylamine, $C_6H_5CH_2NH_2$, respectively. Its various properties have already been discussed on page 2·514.

13. **Benzylidene chloride, $C_6H_5CHCl_2$.**—It may be prepared industrially—

(*i*) *By passing chlorine through boiling toluene in presence of light until the requisite increase in weight is obtained.*

$$\underset{\text{Toluene}}{C_6H_5CH_3+2Cl_2} \longrightarrow \underset{\text{Benzylidene chloride}}{C_6H_5.CHCl_2} + 2HCl \qquad (g)$$

(*ii*) *By the action of phosphorus pentachloride on benzaldehyde*

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO}+PCl_5 \longrightarrow \underset{\text{Benzylidene chloride}}{C_6H_5CHCl_2} + POCl_3$$

It is a colourless liquid (b.p. 480K) which is hydrolysed to benzaldehyde by calcium hydroxide solution.

$$C_6H_5CHCl_2+Ca(OH)_2 \longrightarrow C_6H_5CHO+CaCl_2+H_2O$$

It is used for the industrial preparation of benzaldehyde.

14. **Benzylidyne chloride, $C_6H_5CCl_3$.**—It may be prepared by passing chlorine through boiling toluene in the presence of light until the corresponding increase in weight takes place.

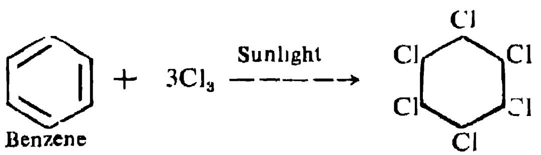
$$C_6H_5CH_3+3Cl_2 \longrightarrow C_6H_5CCl_3+3HCl$$

It is a colourless liquid (b.p. 487 K) which, when heated with calcium hydroxide, gives benzoic acid.

$$C_6H_5CCl_3+2H_2O \xrightarrow{Ca(OH)_2} C_6H_5COOH + 3HCl$$

It is used for the industrial preparation of benzoic acid.

15. **Benzene hexachloride, $C_6H_6Cl_6$.**—This is 1, 2, 3, 4, 5, 6-hexachlorocyclohexane obtained by heating benzene with chlorine in presence of sunlight. Addition takes place by free radical mechanism.



Benzene

Benzene hexachloride

It can exist in eight stereoisomeric forms due to difference in arrangement of H and Cl atoms on opposite sides of the ring. One of these isomers called γ-isomer is a powerful insecticide and acts more quickly than DDT. The product obtained by chlorination of benzene in the presence of ultraviolet light contains 12-14% of the γ-isomer. It is sold under the name *gammaxane*, an insecticide.

17. **Transition from ortho-para to meta Orientation.**—Methyl group in toluene is *o*- & *p*-directing. Progressive replacement of hydrogen atoms of the methyl group by chlorine brings about a

gradual decrease in electron density on the ring and a transition from *ortho-para-* to *m*-orientation. For example, percentages of the meta-nitro-derivative obtained during nitration of these are given below :

$C_6H_5CH_3$	$C_6H_5CH_2Cl$	$C_6H_5CHCl_2$	$C_6H_5CCl_3$
2-5%	10-15%	30-35%	60-65%

QUESTIONS

Essay Type :

1. How will you introduce chlorine into the side-chain or nucleus to form a chlorine substitution product of an aromatic hydrocarbon ? How do the nuclear substituted compounds differ from the corresponding aliphatic compounds ?

2. Name the isomers having the formula C_7H_7Cl. How would you obtain and distinguish between them ?

3. Write notes on the reactivity of bromine in (*i*) Vinyl bromide, (*ii*) Bromotoluenes, and (*iii*) Benzyl bromide.

4. (*a*) Give electronic mechanisms for the following :

(*i*) Chlorination of benzene.

(*ii*) Chlorine in chlorobenzene on one hand is *o*, *p*-directing and on the other hand deactivates the benzene nucleus towards electrophilic substitution.

(*iii*) Activation of halogen atom attached to the nucleus by the presence of a nitro or carboxyl group in the ortho- or para-position.

(*iv*) Chlorobenzene is not reactive like ethyl chloride but benzyl chloride is as reactive as ethyl chloride.

(*b*) The chlorine atom in chlorobenzene is very much less reactive than in ethyl chloride. Explain why. (*Delhi B.Sc. 1974*)

5. Write a short note on DDT.

6. Starting from toluene, how would you obtain benzyl chloride, benzylidene chloride and benzylidyne chloride ? Give equations. How does benzyl chloride differ from (*a*) chlorotoluenes and (*b*) benzoyl chloride ?

7. (*a*) How would you prepare chlorotoluene from toluene ? Discuss the mechanism of the reaction.

(b) Explain the conditions in which chlorine enters the side chain in toluene. How do these products differ from chlorotoluenes ? (*Nagpur B.Sc. 1973*)

8. Give the methods of preparation and chemical properties of chlorobenzene. (*Delhi B.Sc. 1978*)

Short Answer Type :

1. State giving equations the action of (*i*) aqueous alkali, (*ii*) ammonia, and (*iii*) oxidising agents on $C_6H_5CH_2Cl$ and $ClC_6H_4CH_3$.

2. How do products formed in chlorination of toluene behave towards caustic soda and oxidising agents ?

3. Give one method of preparation of iodobenzene. What are the products obtained when iodobenzene is reacted with chlorine and alkali added to the product ? (*Kerala B.Sc. 1973*)

4. Write an explanatory note on inert character of chlorine in chlorobenzene. (*Delhi B.Sc. 1976*)

5. Give mechanism of chlorination of benzene. How is chlorobenzene obtained on a large scale ? (*Delhi B.Sc. 1976 Supp.*)

6. Explain why chlorobenzene is not acted upon by aqueous NaOH solution and alcoholic ammonia under ordinary conditions. (*Delhi B.Sc. 1976 Supp.*)

7. Account for the fact that 2, 4-Dinitrochlorobenzene is more reactive than chlorobenzene when treated with sodium hydroxide. (*Calicut B.Sc. 1973*)

8. Write equations for the following reactions :

(*i*) Chlorination of cold benzene in presence of iron.

(*ii*) Bromination of cold toluene in presence of iron.

(*iii*) Iodination of benzene in presence of nitric acid.

(*iv*) Phenol+phosphorus pentachloride.

9. What happens when Benzenediazonium chloride reacts with (*i*) cuprous chloride in hydrochloric acid ; (*ii*) cuprous bromide in hydrobromic acid ; (*iii*) potassium iodide ?

10. Write equations for the following reactions :

(*i*) Chlorination of boiling toluene in presence of light.

(*ii*) Phosphorus pentachloride+(*i*) benzyl alcohol ; (*ii*) benzaldehyde.

(*iii*) Phenyl bromide heated with (*i*) aqueous alkali under pressure ; (*ii*) aqueous ammonia in presence of cuprous oxide under pressure, (*iii*) cuprous cyanide in presence of quinoline.

(*iv*) *o*- & *p*-chloronitrobenzene heated with (*i*) alcoholic potash ; (*ii*) alcoholic ammonia.

(*v*) Reduction of chlorobenzene.

11. Write equations for the following reactions :

(*a*) Benzyl chloride+(*i*) aqueous potash ; (*ii*) alcoholic ammonia ; (*iii*) potassium cyanide ; (*iv*) benzene and anhydrous aluminium chloride.

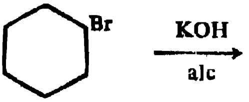
(*b*) Oxidation of (*i*) benzyl chloride ; (*ii*) *o*-chlorotoluene.

(*c*) Conversion of benzene into *m*-chlorotoluene.

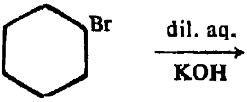
(*d*) Calcium hydroxide+(*i*) Benzylidene chloride ; (*ii*) Benzylidyne chloride.

12. Name the starting material and the product of the reaction. Write N.R. where no reaction occurs. State the type of mechanism of reaction involved in each case.

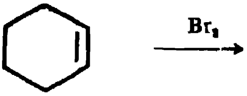
(*a*)



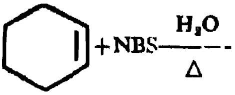
(*b*)



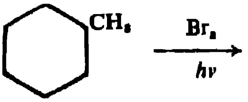
(*c*)



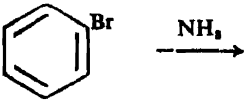
(*d*)



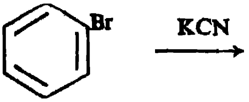
(*e*)



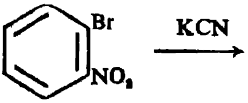
(*f*)



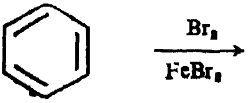
(*g*)



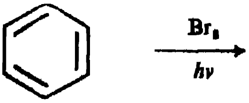
(*h*)



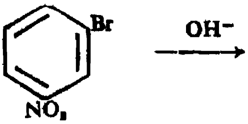
(*i*)



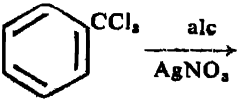
(*j*)



(*k*)



(*l*)

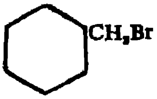


[**Hints.** (*a*) Bromocyclohexane→cyclohexene, E_2.

(*b*) Bromocyclohexane→Cyclohexanol, S_N2

(*c*) Cyclohexene→trans-1, 2-dibromocyclohexane, electrophilic addition of Br_2 to double bond.

(*d*) HOBr produced adds to double bond (*e*)



(*f*) and (*g*) N R (*h*) Br replaced by CN

(*i*) Bromobenzene. (*j*) N.R. (*k*) N R (*l*) AgCl ppt. obtained.

13 Why does side-chain halogenation of toluene proceed *via* free radical mechanism ?

14 How is benzyl radical stabilized ?

15 Give an orbital overlap diagram to represent delocalization of odd electron in benzyl radical

16 Give the resonance hybrid structure of benzyl radical

17 Is side-chain halogenation possible in 4 methylphenol ?

18 What is the utility of NBS in free radical bromination of toluene ? What is the effect of presence of water on the reaction ?

19. What happens when 2-pentene is treated with NBS in dry CCl_4 ?

20 Discuss the elimination-addition mechanism involved in the conversion of chlorobenzene to aniline

21 What is benzyne ? What is its structure ?

22 Name the mechanism involved in the formation of benzene hexachloride from benzene

23 Explain electronically why chlorine atom in chlorobenzene is less reactive than chlorine atom in benzyl chloride *(Delhi B Sc. 1978)*

Problems :

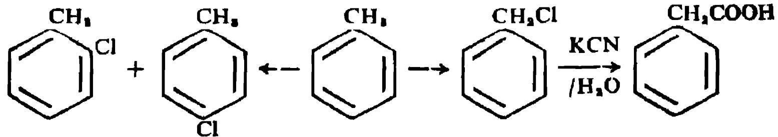
1 On monochlorination C_7H_8 (A) gives according to reaction conditions either B or C and D B on treatment with KCN followed by hydrolysis gives $C_8H_8O_2$ (L) Identify the various compounds A to E

2 The compound C_8H_9Cl (A) on treatment with KCN followed by hydrolysis gives $C_9H_{10}O_2$ (B) Ammonium salt of B on dry distillation yields C which reacts with alkaline solution of bromine to give $C_8H_{11}N$ (D)

Another compound $C_8H_{10}O$ (E) is obtained by the action of nitrous acid on D or by the action of aqueous potash on A E on oxidation gives $C_8H_6O_4$ (F) which gives the inner anhydride $C_8H_4O_3$ (G) on heating. Identify the various compounds A to G.

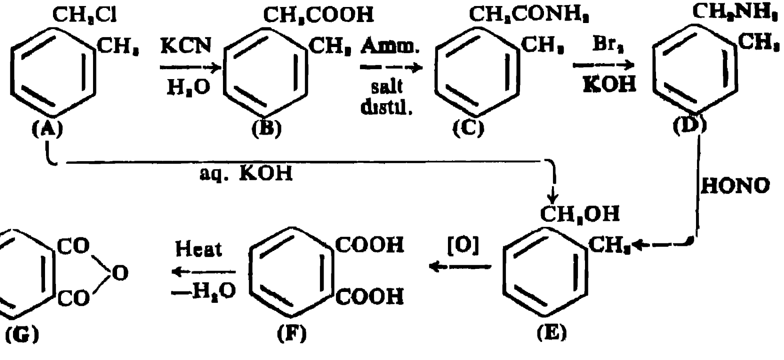
ANSWERS

1



o-Chloro-toluene (C) *p*-chloro-toluene (D) Toluene (A) Benzyl chloride (B) Phenylacetic acid (E)

2.



38

Sulphonic Acids

1. Sulphonation.—One of the most characteristic properties of aromatic hydrocarbons and their derivatives, which differentiate them from aliphatic compounds, is their behaviour towards concentrated sulphuric acid. Benzene when heated with concentrated sulphuric acid forms benzenesulphonic acid by the replacement of one hydrogen atom by a sulphonic group, $-SO_3H$ or $-SO_2.OH$.

The process of replacement of one or more hydrogen atoms of the benzene nucleus by sulphonic groups is known as **sulphonation.** Different methods used for sulphonation are :

(*a*) *By heating the substance with concentrated sulphuric acid or oleum (fuming sulphuric acid).*

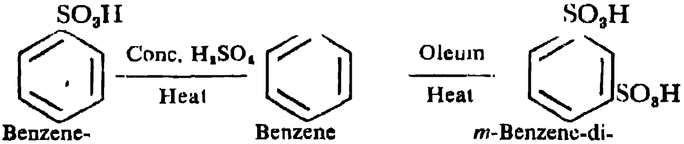
$$\underset{\text{Benzene}}{C_6H_5\boxed{H + HO}}\underset{\text{Sulphuric acid (conc.)}}{SO_3H} \rightleftharpoons \underset{\text{Benzenesulphonic acid}}{C_6H_5.SO_3H} + H_2O$$

For mechanism of sulphonation refer to page 2·480

The number of sulphonic groups which are introduced depends upon :

(*i*) Temperature, (*ii*) Concentration of the acid, and
(*iii*) Nature of the compound sulphonated.

For example, in the above cases benzene with concentrated sulphuric acid gives benzenesulphonic acid. With oleum it gives *m*-benzene disulphonic acid (Two $-SO_3H$ groups are introduced).



Benzene-sulphonic acid Benzene *m*-Benzene-di-sulphonic acid

In all, a maximum of three sulphonic groups can be introduced in benzene, the trisulphonic acid is obtained by continued heating of benzene with oleum.

Presence of groups like $-CH_3$, $-NH_2$, $-OH$, etc., in the nucleus helps sulphonation while presence of $-COOH$ or $-SO_3H$ group, retards it. Very few catalysts are known for sulphonation—the salts of mercury, silver and vanadium and iodine appear to be the best.

(*b*) *By treating the substance with chlorosulphonic acid and carrying out the reaction in carbon tetrachloride solution.*

$$\underset{\text{Benzene}}{C_6H_5|H} + \underset{\text{Chlorosulphonic acid}}{Cl|SO_3H} \longrightarrow \underset{\text{Benzenesulphonic acid}}{C_6H_5SO_3H} + HCl$$

Sulphonic acid is obtained when one molecule of chlorosulphonic acid has been used while excess of the reagent results in the formation of sulphonyl chloride.

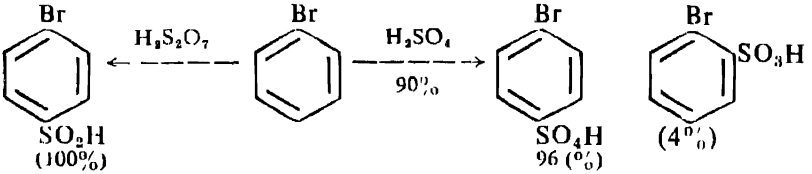
$$\underset{\text{Benzenesulphonic acid}}{C_6H_5.SO_3H} + \underset{\text{Chloro-sulphonic acid}}{ClSO_3H} \rightarrow \underset{\text{Benzenesulphonyl chloride}}{C_6H_5.SO_2Cl} + H_2SO_4$$

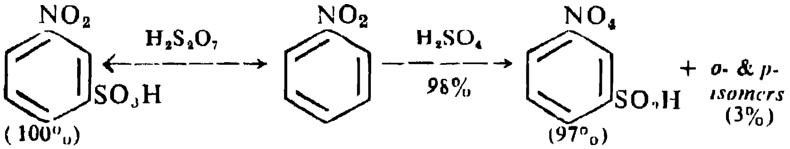
(c) *By treating the aromatic compound with sulphuryl chloride in presence of anhydrous aluminium chloride* when a sulphonyl chloride is obtained.

$$ArH + SO_2Cl_2 \xrightarrow{AlCl_3} ArSO_2Cl + HCl$$

When a compound having an *o*- and *p*-directing group is sulphonated with sulphuric acid or oleum, the temperature of the reaction affects the ratio of the yields of the *o*- and *p*-isomers. *Lower temperatures in general favour o-substitution while higher temperatures favour p-substitution.* A mixture of the *o*- and *p*-isomer is however, obtained every time.

Presence of water also affects the ratio of the various isomers. With concentrated sulphuric acid (98%) the product is either *o*- & *p*-isomers with a little of the *m*-isomer or it is mainly the *m*-isomer with a little of *o*- and *p*-isomers. With oleum the yield is either 100% *ortho* and *para* or *meta*. For example, in sulphonation of bromobenzene or nitrobenzene., we have





2. Isolation of Sulphonic acids.—Sulphonic acids are very soluble in water and non-volatile. This makes their isolation very difficult. Some of the methods employed for their isolation are :

(*i*) When the sulphonic acid is not very soluble, it is isolated by cooling the sulphonating mixture and filtering through glass wool.

(*ii*) In some cases sodium sulphonate is precipitated by allowing the sulphonating mixture to flow into a saturated solution of sodium chloride (*cf.* salting out of soap).

(*iii*) In another method commonly used, the sulphonating mixture is neutralized with lead carbonate. Insoluble lead sulphate is filtered off and the soluble lead salt of sulphonic acid is decomposed with hydrogen sulphide and filtered. The filtrate is evaporated to dryness under reduced pressure.

3. Physical Properties of Sulphonic Acids.—As expected from their structure the physical properties are characteristic of highly polar compounds. They are more soluble in water than in organic solvents. In aqueous solution they are completely ionized.

$$ArSO_3H + H_2O \longrightarrow ArSO_3^- + H_3O^+$$

They are also soluble in certain other polar solvents including sulphuric acid, but insoluble in the usual organic solvents. These are compounds with low volatility and generally decompose before the boiling points are reached. Since these are highly deliquescent and difficult to purify, these are conveniently prepared as salts and used in this form.

4. Reactions of Sulphonic acids.—The more important reactions of aromatic sulphonic acids are summarized below :

(1) **Reactions involving H-atom of the —SO$_3$H group (Salt formation).**

$$ArSO_3H + H_2O \rightarrow ArSO_3^- + H_3O^+ \quad \textit{(Completely ionized)}$$

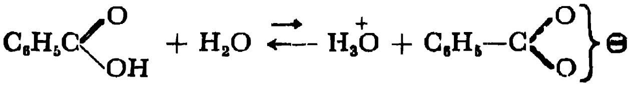
They neutralize alkalis, decompose carbonates and dissolve metals—H-atom is replaced by the metal radical.

$$2ArSO_3H + 2Na \rightarrow \underset{\text{Sodium salt}}{2ArSO_3Na} + H_2$$

$$ArSO_3\boxed{H + HO}K \rightarrow \underset{\text{Potassium salt}}{Ar\,SO_3K} + H_2O$$

$$2ArSO_3H + Na_2CO_3 \rightarrow 2ArSO_3Na + CO_2 + H_2O$$

We have seen that the carboxylic acids owe their appreciable acidity to the effect of the acyl group RCO—. On the release of H$^+$ from the —OH group, the negative charge of the carboxylate anion is dispersed over two oxygen atoms.

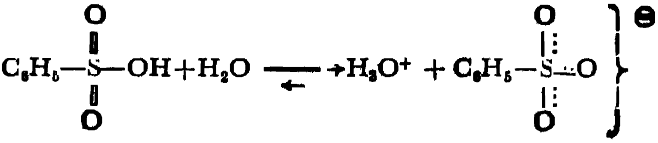


$$C_6H_5C\begin{matrix}\nearrow O\\ \searrow OH\end{matrix} + H_2O \rightleftharpoons \overset{+}{H_3O} + C_6H_5{-}C\left\{\begin{matrix}O\\ O\end{matrix}\right\}^{\ominus}$$

In the same way sulphonic acids owe their powerful acidity to the effect of sulphonyl group, ArSO$_2$—. Greater acidity of sulphonic acids as compared with carboxylic acids is due to—

(*i*) presence of two different elements in the two groups—sulphur in sulphonyl group (ArSO$_2$—) and carbon in carbonyl group, RCO— or ArCO—) and

(*ii*) the fact that in sulphonyl group there are two oxygen atoms to help accommodate the negative charge of the anion and only one oxygen in the acyl group. The negative charge of sulphonate is dispersed over *three* oxygen atoms :



$$C_6H_5{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}OH + H_2O \rightleftharpoons H_3O^+ + \left[C_6H_5{-}\overset{\overset{O}{\vdots}}{\underset{\underset{O}{\vdots}}{S}}\text{---}O\right]^{\ominus}$$

Although two oxygen atoms of the sulphonyl group promote the ionization of hydrogen they appear to make the replacement of the —OH group more difficult. Thus only its replacement by Cl directly is possible : esters and amides have to be prepared indirectly from the sulphonyl chloride.

(2) **Reactions involving —OH group of the sulphonic group (SO_2OH)** .

(a) With phosphorus halides, *e.g.*, phosphorus pentachloride, the —OH group is replaced by a halogen atom.

$$\underset{\text{Benzenesulphonic acid}}{C_6H_5SO_2OH} + PCl_5 \rightarrow \underset{\text{Benzenesulphonyl chloride}}{C_6H_5SO_2Cl} + POCl_3 + HCl \qquad (g.\text{-}ex)$$

(b) *Dehydration.* Sulphonic acid anhydrides have been prepared by heating the acid with excess of phosphorus pentoxide.

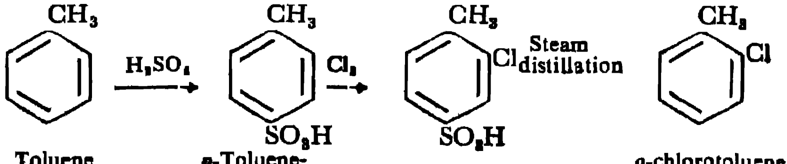
$$2C_6H_5.SO_2OH \xrightarrow[-H_2O]{P_4O_{10}} (C_6H_5SO_2)_2O \qquad (70\%)$$

(3) **Reactions involving the whole of —SO_3H group.**

(a) *Desulphonation or Hydrolysis.* Sulphonation reactions are reversible as explained on page *2·480*. Sulphonic acid can, therefore, be readily desulphonated, *i.e.*, hydrolysed. It is not hydrolysed by heating with aqueous alkali or mineral acid. But on boiling with dilute hydrochloric acid under pressure at 420-470K, it gives benzene by hydrolysis.

$$C_6H_5\boxed{SO_3H + HO}H \xrightarrow[420K]{HCl} \underset{\text{Benzene}}{C_6H_6} + H_2SO_4 \qquad (v.g.)$$

In some cases the sulphonic acid group may be eliminated by mere steam distillation. This makes sulphonation useful in the preparation of certain compounds. For example, *o*-chlorotoluene is prepared as follows :



Toluene *p*-Toluene-sulphonic acid *o*-chlorotoluene

(b) ***With Solid Alkalis.*** The acids or their sodium salts on fusion with solid alkalis give **phenols.**

$$\underset{\text{Sodium benzene-sulphonate}}{C_6H_5\boxed{SO_3Na + Na}} \underset{(\textit{Solid})}{OH} \xrightarrow{\text{Fuse}} \underset{\underset{\text{Sodium phenoxide}}{\underset{C_6H_5ONa}{\text{HCl} \uparrow \downarrow \text{NaOH}}}}{\underset{\text{Phenol}}{C_6H_5OH}} + Na_2SO_3 \qquad (g.\text{-}v.g.)$$

(c) ***With Metallic Cyanides.*** Sodium or potassium salts of the acids when fused with a metallic cyanide give aryl cyanide which can further give aromatic amines and aromatic acids on reduction and hydrolysis respectively.

$$\underset{\text{Pot. benzene-sulphonate}}{C_6H_5\boxed{SO_3K + K}}CN \longrightarrow \underset{\text{Phenyl cyanide}}{C_6H_5CN} + K_2SO_3 \qquad (f.g.)$$

$$\underset{\text{Benzylamine}}{C_6H_5CH_2NH_2} \xleftarrow{4H} \underset{\substack{\text{Phenyl-}\\\text{cyanide}}}{C_6H_5CN} \xrightarrow[-NH_3]{\text{Hydrolysis}} \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

(*d*) *With Sodamide*. Sodium salts of the acid, when fused with sodamide, give amino-compounds.

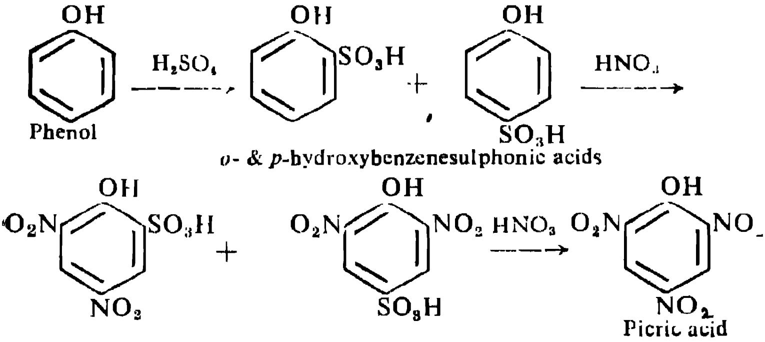
$$C_6H_5\overline{SO_3Na + Na}|NH_2 \longrightarrow \underset{\text{Aniline}}{C_6H_5NH_2} + Na_2SO_3 \quad (\text{f.g.-g.})$$

Sodamide

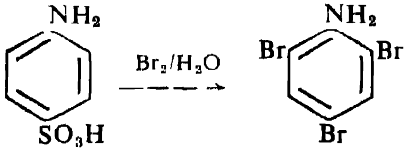
(*e*) *With Potassium hydrogen sulphide*. Potassium salts of sulphonic acids when fused with potassium hydrogen sulphide give *thiophenols*.

$$\text{Ar}\,\boxed{\;\text{[illegible]}\;}\,\text{SH} \dashrightarrow \underset{\text{Thiophenol}}{\text{ArSH}} + K_2SO_3 \qquad (\text{f. g.})$$

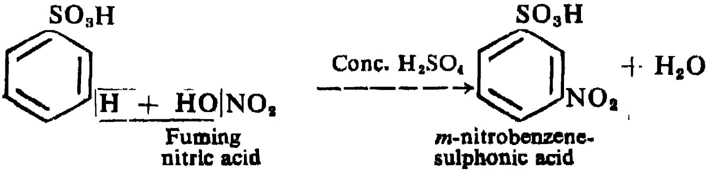
(*f*) *Replacement of sulphonic group by Nitro group*. Very often the sulphonic group is readily replaced by nitro group. Nitro derivatives of compounds which are easily oxidised by nitric acid are first sulphonated and then nitrated. For example, phenol is coverted into picric acid as follows :

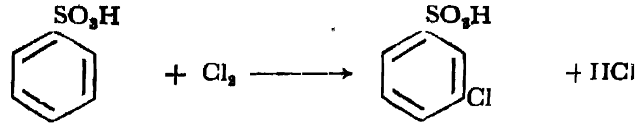


(*g*) *Replacement by Halogen atom*. Sulphonic group present in a position *o*- and *p*- to a hydroxyl or amino group can be replaced by a halogen atom. For example, sulphanilic acid forms *s*-tribromo-aniline when treated with bromine.



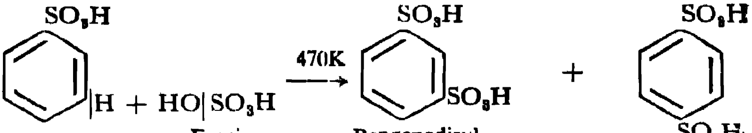
(4) **Reactions of the Benzene Nucleus.** It can be nitrated, halogenated and further sulphonated forming meta derivative in each case, as the main product.





Benzenesulphonic acid

m-chlorobenzene-sulphonic acid

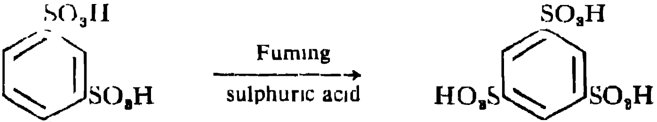


Fuming sulphuric acid

m-Benzenedisulphonic acid (*main product*)

(*small amount*)

Continued heating of the *m*-isomer with sulphuric acid results in its rearrangement to the *p*-isomer. *s*-Benzenetrisulphonic acid is obtained by heating benzene *m*-disulphonic acid with fuming sulphuric acid.



m-benzene-disulphonic acid

s-Benzene-trisulphonic acid

Uses. Due to the ease with which the sulphonic group can be replaced by other groups, sulphonic acids are valuable synthetic reagents. Further, since the presence of a sulphonic group makes the compound soluble in water, sulphonation is an extremely important process in the manufacture of dyes and drugs.

5. Benzenesulphonic Acid, $C_6H_5.SO_3H$.

Preparation. Benzenesulphonic acid can be readily prepared by heating benzene with concentrated sulphuric acid at 350K.

$$\underset{\text{Benzene}}{C_6H_5\,H} + \underset{\text{Sulphuric acid}}{HO|SO_3H} \rightleftharpoons \underset{\text{Benzenesulphonic acid}}{C_6H_5.SO_3H} + H_2O \qquad (75\text{-}80\%)$$

The reaction is reversible and removal of water from the reaction mixture is, therefore, necessary to obtain the maximum yield. This may be done by using oleum ($H_2S_2O_7$ or $H_2SO_4+SO_3$) which removes water chemically.

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

Alternatively, the reaction is carried out at higher temperatures or under reduced pressure.

Expt. A mixture of benzene (1 part) and concentrated sulphuric acid (2 parts) is taken in a round-bottom flask fitted with reflux condenser and heated on a sand bath until whole of beneczne is dissolved. The reaction mixture is poured in water and treated with barium carbonate (*excess*) when unused sulphuric acid is precipitated as barium sulphate and filtered off. Benzenesulpshonic acid forms its barium salt which, being soluble, remains in solution.

$$H_2SO_4 + BaCO_3 \rightarrow \underset{\text{Insoluble}}{BaSO_4} + CO_2 + H_2O$$

$$2C_6H_5SO_3H + BaCO_3 \rightarrow \underset{\substack{\text{Barium benzene-}\\ \text{sulphonate (}\textit{soluble}\text{)}}}{(C_6H_5SO_3)_2Ba} + CO_2 + H_2O$$

The filtrate is treated with dilute sulphuric acid (calculated quantity) to regenerate benzenesulphonic acid. This is concentrated to crystallization on a water bath and crystals obtained.

For Manufacture of Benzenesulphonic acid, the same method is employed with the only difference that the operation is carried out in a steam-jacketed pan fitted with a mechanical stirrer.

Properties : Physical. It is a colourless, crystalline substance (m.p. 317K) crystallizing with 1½ molecule of water. The anhydrous acid melts at 288K. It is very deliquescent and highly soluble in water and alcohol. The solution is strongly acidic (about as strong as sulphuric acid). Its barium and lead salts are soluble in water.

6. Benzenesulphonyl Chloride, $C_6H_5SO_2Cl$.

Preparation. It can be prepared by heating benzenesulphonic acid or its salt with phosphorus pentachloride on a water bath.

$$\underset{\substack{\text{Benzenesulphonic}\\ \text{acid}}}{C_6H_5.SO_2OH} + PCl_5 \rightarrow \underset{\substack{\text{Benzenesulphonyl}\\ \text{chloride}}}{C_6H_5SO_2.Cl} + POCl_3 + HCl \qquad (g.\text{-}ex.)$$

$$\underset{\text{Sodium salt}}{C_6H_5SO_2.ONa} + PCl_5 \rightarrow C_6H_5.SO_2Cl + POCl_3 + NaCl \quad (75\text{-}80\%)$$

It is, however, usually prepared by treating benzene with chlorosulphonic acid (*excess*).

$$C_6H_6 + 2Cl.SO_3H \rightarrow C_6H_5\ SO_2Cl + H_2SO_4 + HCl \qquad (75\text{-}77\%)$$

Properties and Uses. It is an oily liquid (b.p. 519K, with decomposition) soluble in ether and having characteristic pungent smell. Chemically it resembles an acid chloride as shown by its reactions.

(*i*) *Hydrolysis.* It is fairly stable and is decomposed only very slowly by water but rapidly by alkali.

$$C_6H_5SO_2\overline{Cl + H}|\underset{\text{Water}}{OH} \longrightarrow \underset{\substack{\text{Benzenesulphonic}\\ \text{acid}}}{C_6H_5SO_2.OH} + HCl$$

(*ii*) *With Alcohols.* It reacts with alcohols in the presence of alkali to form esters.

$$C_6H_5SO_2\underline{|Cl + H}|\underset{\text{Ethanol}}{OC_2H_5} + NaOH \rightarrow \underset{\substack{\text{Ethyl benzene-}\\ \text{sulphonate (}\textit{Ester}\text{)}}}{C_6H_5SO_3C_2H_5} + NaCl + H_2O$$

(*iii*) *With Ammonia.* When shaken with concentrated ammonia, benzenesulphonyl chloride gives benzenesulphonamide.

$$C_6H_5SO_2Cl + 2NH_3 \rightarrow \underset{\text{Benzenesulphonamide}}{C_6H_5SO_2NH_2} + NH_4Cl$$

(*iv*) *With Amines.* It reacts with primary and secondary amines to form *N*-substituted sulphonamides.

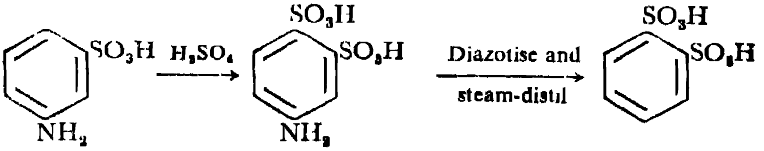
$$RNH_2 + ClSO_2C_6H_5 \longrightarrow \underset{\substack{N\text{-alkylbenzene-}\\ \text{sulphonamide}\\ (\textit{Soluble in alkali})}}{RNH.SO_2C_6H_5} + HCl$$

$$R_2N\underline{|H + Cl}SO_2C_6H_5 \longrightarrow \underset{\substack{N,\,N\text{-dialkylbenzene-}\\ \text{sulphonamide}\\ (\textit{Insoluble in alkali})}}{R_2N.SO_2C_6H_5} + HCl$$

This reaction is used for the separation of primary, secondary and tertiary amines (*Hinsberg's method*, chapter 27).

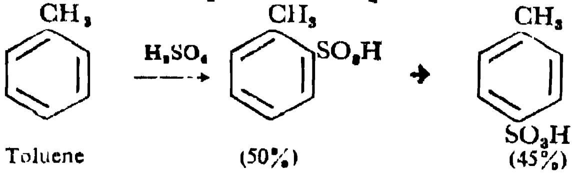
7. **Benzenedisulphonic Acids.**—On heating benzene with excess of fuming sulphuric acid at 470K, we get benzene-*m*-disulphonic acid (main product) and a small amount of the *p*-isomer. Continued heating of the *m*-isomer in sulphuric acid causes it to rearrange to the *p*-isomer.

Benzene-*o*-disulphonic acid cannot be prepared directly. It is obtained from *m*-amino-benzenesulphonic acid as follows :

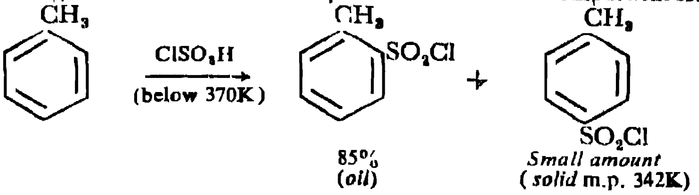


When fused with solid KOH both *m*- and *p*-benzenedisulphonic acids form resorcinol whereas the *o*-isomer gives catechol.

8. **Toluenesulphonic Acids**.—When toluene is sulphonated with concentrated sulphuric acid a mixture of *o*- and *p*-toluenesulphonic acid is obtained. Low temperatures (below 370K) favour the formation of the *o*-isomer while high temperatures (above 370K) favour the formation of the *p*-isomer.



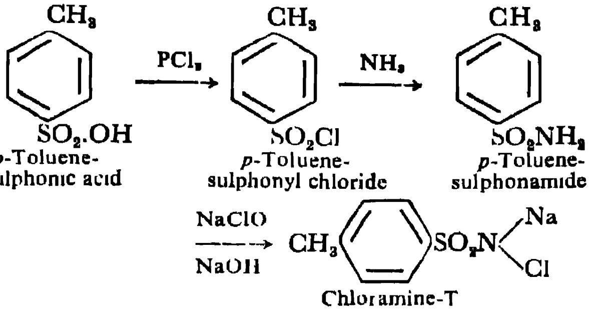
A much better yield of the *o*-isomer may be obtained by sulphonating toluene with chlorosulphonic acid at low temperatures.

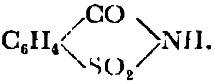


The two chlorides are separated by filtration and converted into the corresponding sulphonic acid by heating with alkali and then acidifying the solution.

For separation of *o*- and *p*-isomers, these are first converted into the sulphonyl chloride and then separated as given above.

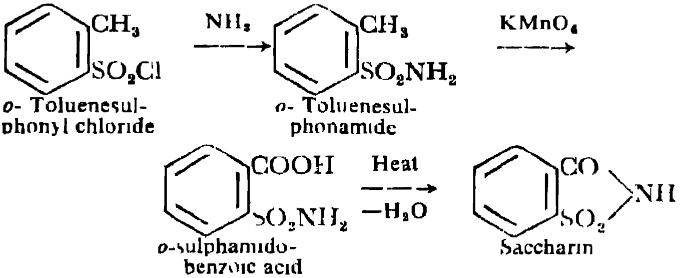
Both *o*- and *p*-isomers are crystalline solids with melting points 340·5K and 379K respectively. *o*-Toluenesulphonyl chloride is used in the manufacture of saccharin and *p*-Toluenesulphonyl chloride is used in the preparation of chloramine-T, an antiseptic.



9. **Saccharin** (*o-sulphobenzoic imide*), 

$$C_6H_4\begin{matrix}CO \\ SO_2\end{matrix}NH.$$

Preparation. Toluene is sulphonated with chlorosulphonic acid and the *o*- and *p*-toluenesulphonyl chlorides are separated by filtration. The *o*-isomer is then treated with ammonia and the resulting amide oxidised with permanganate when we get *o*-sulphamidobenzoic acid which on heating gives saccharin.



Pure saccharin is obtained in greater yield by oxiding *o*-toluene sulphonamide with $K_2Cr_2O_7 + H_2SO_4$.

Properties and Uses. It is a crystalline solid (m.p. 497K) about 550 times as sweet as sugar. It is nearly insoluble in water but its sodium salt is very soluble. It is, therefore, sold as its sodium salt. In very dilute solution it tastes sweet but the concentrated solutions taste bitter. It has no food value and is excreted unchanged in urine.

It is used as sweetening agent in cheap drinks and by diabetic patients and for persons who are not permitted to use sugar.

QUESTIONS

Essay Type :

1. What is sulphonation ? Describe the preparation of aromatic sulphonic acids and give their important reactions. What are the uses of sulphonation ? How can saccharin be prepared from toluene ? (*Ravi Shankar B.Sc. 1972*)

2. How will you obtain a pure sample of benzenesulphonic acid in the laboratory ? What happens when it is (*i*) fused with NaOH, (*ii*) treated with

phosphorus pentachloride, (*iii*) fused with sodamide, (*iv*) treated with steam under pressure ? (*Delhi B.Sc. 1976*)

3. Describe with essential practical details for the preparation of benzenesulphonic acid. How will you prepare from it

(*i*) benzonitrile, (*ii*) phenol, (*iii*) benzoic acid
(*iv*) benzene, (*v*) benzenesulphonamide, (*vi*) thiophenol,
(*vii*) phenyl cyanide, and (*viii*) benzenesulphonyl chloride ?
(*Delhi B.Sc. 1971* ; *Ravi Shankar 1972* ; *Mysore 1970*)

4. Discuss the structure of benzenesulphonic acid. What are its properties ?

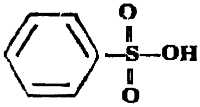
[**Hint :** Structure of benzenesulphonic acid follows from its properties. For example,

(*i*) It contains an acidic H-atom. [—Reaction (1)

(*ii*) There is one —OH group. [—Reaction (2)]

(*iii*) Sulphonic group is a monovalent group shown by its replacement by other monovalent groups.

From the above, structure of benzenesulphonic acid is—



5. How can benzenesulphonyl chloride be prepared ? What are its important properties ? Describe its importance in the separation of a mixture containing primary, secondary and tertiary amines.

hort Answer Type :

1. What is sulphonation ?

2. Name various methods used for sulphonation. Write a chemical equation for each.

3. On what factors does the number of sulphonic groups introduced during sulphonation depend ?

4. Write mechanism of sulphonation of benzene.

5. How do you explain greater acidity of sulphonic acids as compared with carboxylic acid ?

6. Why are sulphonic acids valuable synthetic reagents ?

7. How is saccharin synthesised ? What is it used for ?

8. Write equations for the reactions, between :

(1) Benzene+(*a*) concentrated sulphuric acid ; (*b*) oleum ; (*c*) chlorosulphonic acid using (*i*) one molecule ; (*ii*) excess ; (*d*) sulphuryl chloride.

(2) Benzenesulphonic acid + (*i*) sodium ; (*ii*) caustic soda solution ; (*iii*) sodium carbonate ; (*iv*) phosphorus pentachloride ; (*v*) dilute hydrochloric acid under pressure at 420-470K ; (*vi*) P_4O_{10}.

(3) Sodium benzenesulphonate+(*i*) solid caustic soda (*fused*) ; (*ii*) sodium cyanide (*distilled*) ; (*iii*) sodamide (*fused*) ; (*iv*) phosphorus pentachloride ; (*v*) KSH.

(4) Nitration, chlorination and further sulphonation of benzenesulphonic acid.

(5) Benzenesulphonyl chloride+(*i*) alkali ; (*ii*) alcohol and sodium hydroxide (*iii*) ammonia ; (*iv*) methylamine ; and (*v*) dimethylamine.

9. How will you bring about the conversion of :

(*a*) Sulphanilic acid into *s*-tribromoaniline.

(*b*) Toluene into (*i*) *o*-chlorotoluene ; (*ii*) chloramine-T ; (*iii*) saccharin.

(*c*) Phenol into picric acid .

10. Explain the mechanism of sulphonation of benzene.

(Osmania B.Sc. 1980)

Hint. Write equations for the following steps involved in the sulphonation of benzene :

(*i*) Production of SO_3 from H_2SO_4.

(*ii*) Formation of σ complex from $C_6H_6+SO_3$.

(*iii*) Abstraction of proton from the σ complex by the base (HSO_4^-) to give $C_6H_5SO_3^-$.

(*iv*) Reaction between $C_6H_5SO_3^-$ and H_3O^+.]

11. Sulphonation is a reversible process. With conc. H_2SO_4 position of equilibrium lies appreciably to the right. With a high concentration of water (on passing steam or with dilute H_2SO_4) equilibrium shifts to the left. It shifts further to left with volatile aromatic compound which distils over with steam.

Show all steps of desulphonation when benzenesulphonic acid is heated with dilute sulphuric acid.

12. In most desulphonation reactions the electrophile is a proton. Other electrophiles may, however, be used.

When benzenesulphonic acid reacts with bromine in presence of $FeBr_3$, bromobenzene is obtained. Name the electrophile in this reaction. Write various steps involved in the mechanism for this reaction.

13. On sulphonation of toluene at 273K and 373K the following proportions of monosubstituted products are obtained :

	ortho	*para*	*meta*
273K	43%	53%	4%
373K	13%	79%	8%

(*a*) Keeping in mind that sulphonation reactions are reversible, how can you account for the difference in the relative proportions of the three products at the lower and higher temperature ?

(*b*) Which toluenesulphonic acid appears to be more stable, ortho or para ?

[**Hint** : (*a*) At lower temperature the reaction is rate controlled ; at the higher temperature it is equilibrium controlled.

(*b*) *p*-toluenesulphonic acid is more stable than *o*-toluenesulphonic acid.

At lower temperatures the relative proportion of ortho and para isomers is determined by the rate constants of the reactions resulting in their formation.

At higher temperatures the ortho-isomer being less stable is decomposed more rapidly. Thus para-isomer accumulates at the cost of ortho- isomer till the equilibrium point is reached.]

Problems :

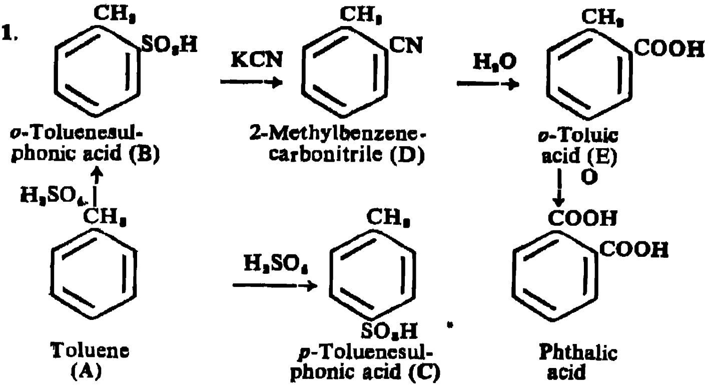
1. An aromatic compound C_7H_8 (A) on sulphonation gives two compounds B and C. The compound B on fusion with KCN gives C_8H_7N (D) which on hydrolysis yields $C_8H_8O_2$ (E) which on oxidation forms phthalic acid. Identify the compounds A to E.

2. On disulphonation followed by fusion with NaOH and acidification, an aromatic compound C_8H_{10} (A) gives two isomeric compounds B and C (molecular formula $C_8H_{10}O_2$). Oxidation of esters of B and C followed by hydrolysis gives two isomeric compounds D and E ($C_7H_6O_4$) which may be decarboxylated to form $C_6H_6O_2$ (F). Identify the compounds A to F.

3. Xylene (A) gives on mono-sulphonation only one substance (B) which on fusion with solid NaOH followed by acidification gives the phenol C. Identify the compounds A to C.

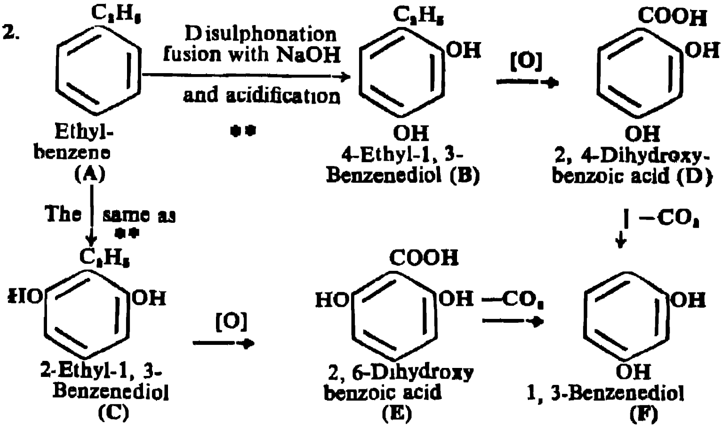
ANSWERS

1.



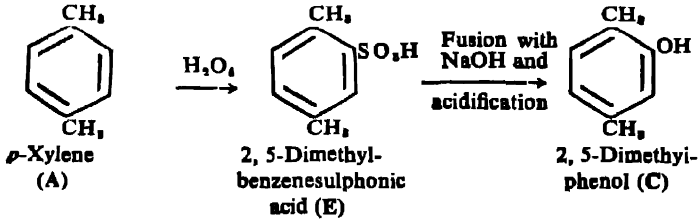
CH₃
SO₃H
KCN
CH₃
CN
H₂O
CH₃
COOH
o-Toluenesulphonic acid (B)
2-Methylbenzenecarbonitrile (D)
o-Toluic acid (E)
O
H₂SO₄
CH₃
COOH
COOH
CH₃
H₂SO₄
SO₃H
Toluene (A)
p-Toluenesulphonic acid (C)
Phthalic acid

2.



C₂H₅
Disulphonation fusion with NaOH and acidification
C₂H₅
OH
[O]
COOH
OH
Ethylbenzene (A)
**
OH
4-Ethyl-1, 3-Benzenediol (B)
OH
2, 4-Dihydroxybenzoic acid (D)
The same as **
–CO₂
C₂H₅
HO
OH
[O]
COOH
HO
OH
–CO₂
OH
2-Ethyl-1, 3-Benzenediol (C)
2, 6-Dihydroxy benzoic acid (E)
OH
1, 3-Benzenediol (F)

3.



CH₃
H₂SO₄
CH₃
SO₃H
Fusion with NaOH and acidification
CH₃
OH
CH₃
CH₃
CH₃
p-Xylene (A)
2, 5-Dimethylbenzenesulphonic acid (E)
2, 5-Dimethylphenol (C)

39

Aromatic Nitro Compounds

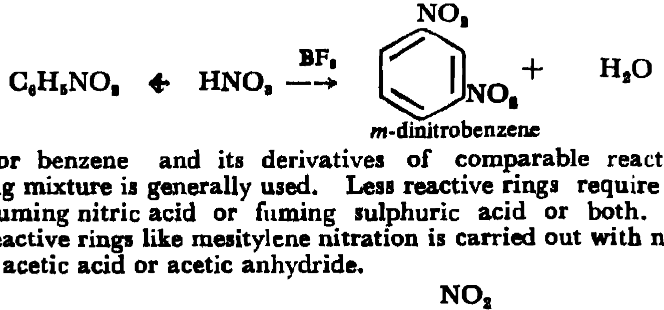
1. Nitration.—One of the characteristic properties of aromatic compounds, which serves to distinguish them from the aliphatic compounds, is the ease with which they react with concentrated nitric acid to form nitro derivatives. In this reaction one or more hydrogen atoms of the nucleus are replaced by nitro groups. The *process of replacement of one or more hydrogen atoms of the benzene nucleus by nitro groups is known as* **Nitration.**

Various reagents used for direct nitration of aromatic compounds are :

(*i*) *Concentrated nitric acid* (Sp. Gr. about 1·5)

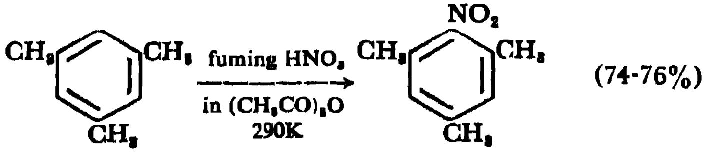
(*ii*) *Fuming nitric acid* (nitrogen dioxide dissolved in concentrated nitric acid).

(*iii*) *Nitrating Mixture.* It is a mixture of nitric acid (concentrated or fuming) with concentrated sulphuric acid. Sulphuric acid serves to protonate HNO_3 and produce nitronium ions ($^+NO_2$). Glacial acetic acid is sometimes used instead of sulphuric acid. Boron trifluoride is an effective catalyst for nitration particularly for nitrating compounds containing a negative group.



m-dinitrobenzene

For benzene and its derivatives of comparable reactivity nitrating mixture is generally used. Less reactive rings require the use of fuming nitric acid or fuming sulphuric acid or both. For more reactive rings like mesitylene nitration is carried out with nitric acid in acetic acid or acetic anhydride.

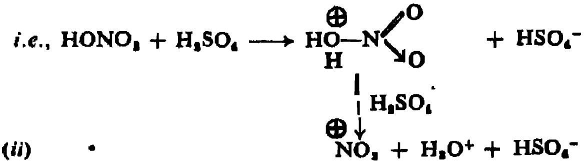


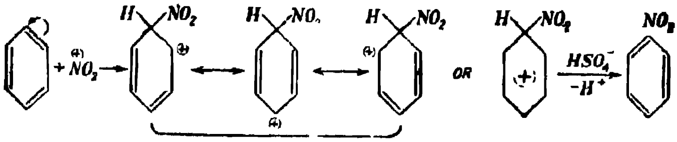
mesitylene nitromesitylene

Experimental work on nitration has shown that nitration with acid mixture is due to nitronium ion believed to be formed (as given under mechanism). The existence of nitronium ion has been confirmed by experiments.

Mechanism of Nitration. Nitration with acid mixture possibly proceeds as follows :

$$(i)\quad HONO_2 + 2H_2SO_4 \rightleftharpoons \underset{\text{Nitronium ion}}{\overset{\oplus}{NO_2}} + H_3O^+ + 2HSO_4^-$$

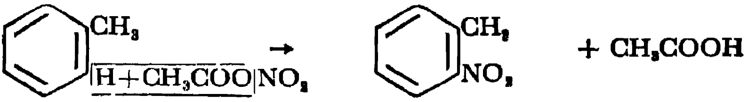




Contributing structures of the intermediate carbocation.

Nitration is an irreversible process as explained on page *2·481.*

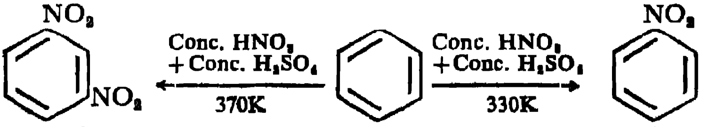
(*iii*) *Acetyl Nitrate,* $CH_3CO.ONO_2$. It has the advantage of introducing only one nitro group which enters the ortho position. It is, however, dangerous to use since it tends to explode when heated.



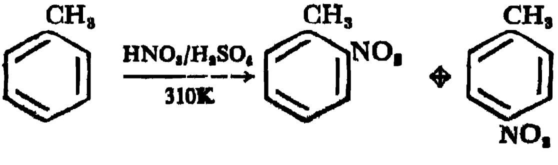
Toluene Acetyl nitrate *o* nitrotoluene

Not more than three nitro-groups can usually be introduced into the benzene nucleus. The actual number of nitro groups introduced depends on :

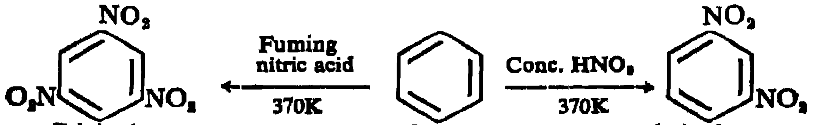
(*i*) **Temperature.** For example, when benzene is treated with concentrated nitric acid+concentrated sulphuric acid, one nitro group is introduced if the mixture is warmed to 330K while two nitro groups enter when the mixture is heated to 370K to give *m*-dinitrobenzene. For mononitration optimum temperature varies from 310K to 330K.



m-dinitrobenzene Benzene Nitrobenzene

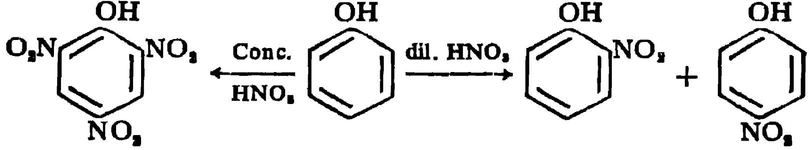


(*ii*) **Nature of the nitrating agent.** For example, concentrated nitric acid at 370K introduces two nitro groups in benzene nucleus while three nitro groups are introduced with fuming nitric acid.



s-Trinitrobenzene Benzene m-dinitrobenzene

(*iii*) **Nature of the substance to be nitrated:** Presence of electron-releasing groups, *e.g.*, $—CH_3$, —OH, $—NH_2$ facilitates nitration. For example, benzene is not affected by dilute nitric acid while phenol gives nitrophenol. Only one nitro group is introduced in benzene with concentrated nitric acid while three nitro groups are introduced in phenol when treated with concentrated nitric acid.



2 : 4 : 6-trinitrophenol Phenol ortho- para-
Nitrophenols

2. General properties of the Nitro compounds.

(*i*) Most of the aromatic nitro compounds are yellow crystalline solids ; the simplest few, including nitrobenzene, are pale-yellow liquids with strong characteristic odour.

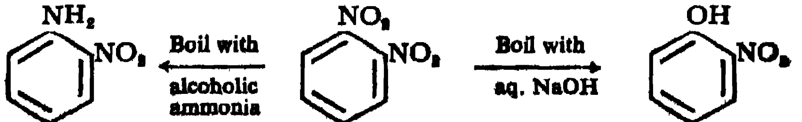
(*ii*) All nitro compounds are denser than water, in which they are insoluble but are soluble in organic solvents. Most of them are volatile in steam.

(*iii*) The melting and boiling points gradually increase with the introduction of nitro groups into the nucleus.

	M.P.	B.P.		M.P.	B.P.
Benzene	278·5K	353K	*m*-Dinitrobenzene	363·8K	576K
Nitrobenzene	278·7K	484K	*s*-Trinitrobenzene	395K	

(*iv*) The polynitro derivatives decompose when strongly heated, often with explosive violence. Thus except for a few mononitro derivatives, these cannot be distilled under atmospheric pressure.

(*v*) In the case of mononitro compounds the nitro group is firmly attached to the nucleus and cannot be easily replaced by other groups. In case of certain di- and polynitro derivatives or halogen-substituted nitro compounds, the nitro groups can, however, be replaced by certain other groups. For example :



o-nitroaniline o-dinitrobenzene o-nitrophenol (*vi*) Their most important reaction is their reduction by various reducing agents (see ***reduction of nitrobenzene***).

INDIVIDUAL MEMBERS

3. Nitrobenzene (Oil of Mirbane), $C_6H_5NO_2$.

Preparation : (*i*) **Laboratory Method.** In the laboratory nitrobenzene is prepared by the nitration of benzene with concentrated nitric and sulphuric acids mixture at a temperature below 330K.

$$\underset{\text{Benzene}}{C_6H_5|H} + \underset{\text{Concentrated}}{HO|NO_2} \xrightarrow{\text{Conc. } H_2SO_4} \underset{\text{Nitrobenzene}}{C_6H_5NO_2} + H_2O$$

Expt. About 50 cm³ of benzene are taken in a round-bottom flask and to this is added very slowly (1 cm³ at a time) a well cooled mixture of concentrated nitric acid (60 cm³) and concentrated sulphuric acid (70 cm³). The flask is shaken and cooled under tap water after each addition. When the whole of acid mixture has been added, the flask is heated on water bath at 325-335K for about an hour. Nitrobenzene forms the upper yellow layer.

It is taken in a separating funnel and the lower acid layer is drawn off. The upper layer is treated with sodium carbonate solution to remove the excess of acid. The lower nitrobenzene layer is drawn off and washed with water several times as before. It is then dried over fused calcium chloride and distilled with an air condenser. The fraction distilling over between 480K and 484K is pure nitrobenzene.

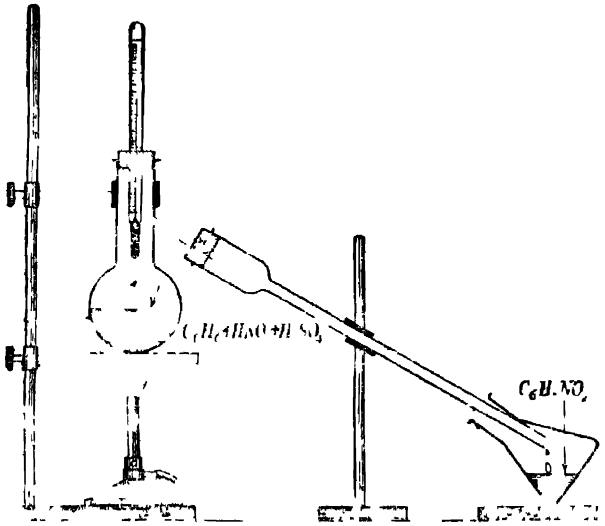


Fig. 39·1—Laboratory preparation of nitrobenzene.

(*ii*) **Manufacture.** The industrial method for the preparation of nitrobenzene is also similar with the difference that here nitration is carried out in the big cast iron pans each fitted with a stirrer and a pipe through which cold water (for cooling) or steam (for heating) can be circulated.

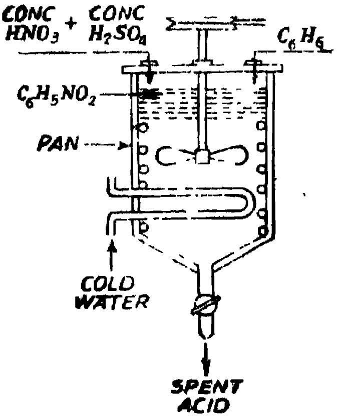


Fig. 39·2—Manufacture of nitrobenzene.

Properties : Physical. Nitrobenzene is a pale yellow oily liquid (b.p. 484K) with a strong smell of bitter almonds. It is insoluble in water, soluble in organic solvents and volatile in steam. Its vapour is poisonous.

Chemical. Nitro group in nitrobenzene is firmly attached to the nucleus and is very inert. It is not replaced by —OH (with aqueous alkali) or —NH$_2$ group (with ammonia). The only reactions given by it are :

(1) **Reduction.** The course of the reduction of nitrobenzene has been shown to take place through the following stages :

$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} \rightarrow \underset{\text{Nitrosobenzene}}{C_6H_5NO} \rightarrow \underset{\text{Phenylhydroxylamine}}{C_6H_5.NHOH} \rightarrow \underset{\text{Aniline}}{C_6H_5NH_2}$$

The nature of the final product, however, depends on the nature of the medium and the nature of the reducing agent. For example,

(*a*) *In Acidic Media.* With metal and acid (Zn+HCl, Sn+HCl or SnCl$_2$+HCl) nitrobenzene is reduced to aniline.

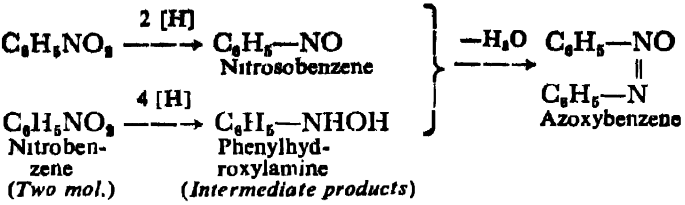
$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} + 6\,[H] \xrightarrow{\text{Metal/acid}} \underset{\text{Aniline}}{C_6H_5NH_2} + 2H_2O$$

The intermediate products, nitrosobenzene and phenylhydroxylamine are reduced far more rapidly than nitrobenzene and so are never isolated.

(*b*) *In Neutral Medium.* With reducing agents like aluminium-mercury couple, zinc dust and ammonium chloride, nitrobenzene is reduced to phenylhydroxylamine. Nitrosobenzene is an intermediate product, not isolated.

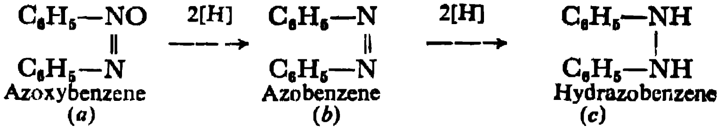
$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} \xrightarrow[-H_2O]{+2H} \underset{\substack{\text{Nitrosobenzene} \\ (\textit{Intermediate product})}}{C_6H_5NO} \xrightarrow{+2H} \underset{\substack{\text{Phenyl-} \\ \text{hydroxylamine}}}{C_6H_5NHOH}$$

(*c*) *In Alkaline Medium.* When reduction of nitrobenzene is carried out in alkaline solution, the reduction products obtained above (C_6H_5NO and C_6H_5NHOH) interact to yield dinuclear products.



$$\left.\begin{array}{l} C_6H_5NO_2 \xrightarrow{2[H]} \underset{\text{Nitrosobenzene}}{C_6H_5{-}NO} \\ \underset{\substack{\text{Nitroben-}\\ \text{zene}\\ (\textit{Two mol.})}}{C_6H_5NO_2} \xrightarrow{4[H]} \underset{\substack{\text{Phenylhyd-}\\ \text{roxylamine}\\ (\textit{Intermediate products})}}{C_6H_5{-}NHOH} \end{array}\right\} \xrightarrow{-H_2O} \underset{\text{Azoxybenzene}}{\begin{array}{c} C_6H_5{-}NO \\ \| \\ C_6H_5{-}N \end{array}}$$

This on further reduction yields azobenzene and hydrazobenzene.



$$\underset{\substack{\text{Azoxybenzene}\\ (a)}}{\begin{array}{c} C_6H_5{-}NO \\ \| \\ C_6H_5{-}N \end{array}} \xrightarrow{2[H]} \underset{\substack{\text{Azobenzene}\\ (b)}}{\begin{array}{c} C_6H_5{-}N \\ \| \\ C_6H_5{-}N \end{array}} \xrightarrow{2[H]} \underset{\substack{\text{Hydrazobenzene}\\ (c)}}{\begin{array}{c} C_6H_5{-}NH \\ | \\ C_6H_5{-}NH \end{array}}$$

By selecting a suitable alkaline reducing agent, any of the three reduction products (*a*), (*b*) and (*c*) can be isolated. For example,

Azoxybenzene is obtained with *alkaline sodium arsenite.*

Azobenzene is prepared by reducing nitrobenzene with *sodium amalgam, alkaline sodium stannite* or best with *zinc dust and methanolic sodium hydroxide.*

Hydrazobenzene is obtained by using *zinc dust and aqueous sodium hydroxide* as reducing agent.

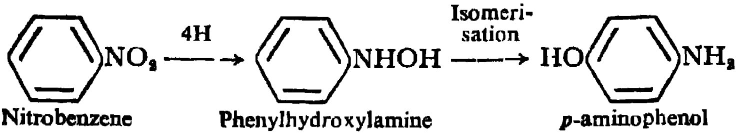
(*d*) *Electrolytic Reduction.* The electrolytic reduction of aromatic nitro compounds was studied by Haber. He observed that the **primary** or **electrolytic reduction products** in both acid and alkaline medium are the same as given above, *i.e.*,

$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} \longrightarrow \underset{\substack{\text{Nitroso-}\\ \text{benzene}}}{C_6H_5NO} \longrightarrow \underset{\substack{\text{Phenylhydro-}\\ \text{xylamine}}}{C_6H_5NHOH} \longrightarrow \underset{\text{Aniline}}{C_6H_5NH_2}$$

The products of these primary reactions then tend to interact with one another, yielding the more complex **secondary** or **chemical reduction** products.

(*i*) A weakly acidic solution of nitrobenzene in alcohol produces aniline. The yield is about 90%.

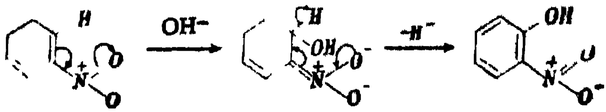
(*ii*) On the other hand, a strongly acidic solution of nitrobenzene yields phenylhydroxylamine as an intermediate product which then isomerises to *p*-aminophenol.



(*iii*) Electrolytic reduction of nitrobenzene in an alkaline medium yields all the mono- and dinuclear reduction products as given above.

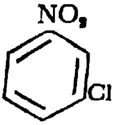
(2) **With solid KOH.** When heated with solid potassium hydroxide, nitrobenzene produces a mixture of *o*- and *p*-nitrophenols and some azoxybenzene.

Presence of electron withdrawing NO_2 group activates the *o*- and *p*- positions for attack by a nucleophile, ^-OH.

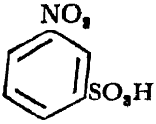


o-Nitrophenol

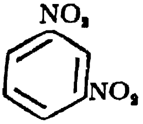
(3) **Properties of the Benzene Nucleus.** Nitrobenzene can be halogenated, sulphonated and further nitrated as usual. The meta derivative is produced in each case.



m-chloronitro-benzene



m-nitrobenzene-sulphonic acid



m-dinitro-benzene

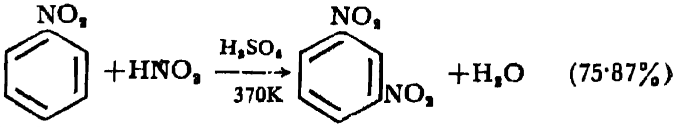
Uses. Nitrobenzene finds use : (*i*) In the manufacture of aniline, benzidine and azo-dyes, etc.

(*ii*) For scenting cheap soaps and shoe polishes under the name *oil of mirbane.*

(*iii*) In the manufacture of floor polishes and as a solvent.

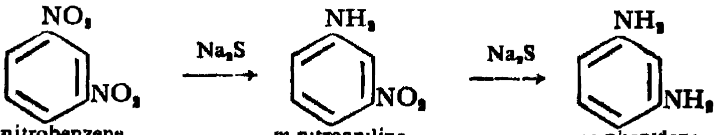
(*iv*) As an oxidising agent in organic synthesis.

4. **Meta-Dinitrobenzene.**—When nitrobenzene (1 part) is heated with a mixture of equal amounts of concentrated sulphuric acid and concentrated nitric acid, the main product is *m*-dinitrobenzene but *o*-isomer is also obtained (about 7%). This is removed during crystallization.



Nitrobenzene *m*-dinitrobenzene

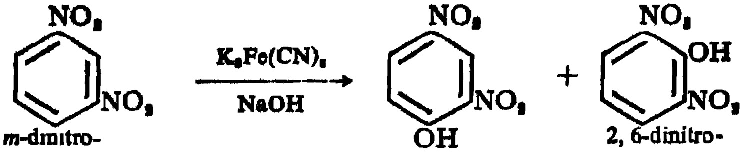
It is a pale-yellow solid (m.p. 363K), practically insoluble in water but readily soluble in alcohol and ether. It is volatile in steam. With sodium sulphide, it is reduced step-wise to *m*-nitroaniline and *m*-phenylenediamine.



m-dinitrobenzene *m*-nitroaniline *m*-phenylene-diamine

Both the nitro groups are rigidly attached to the nucleus and are not replaced by other atoms or groups (*cf.* *o*-dinitrobenzene in which one $-NO_2$ is readily replaced by $-OH$ or $-NH_2$).

With an alkaline solution of $K_3Fe(CN)_6$ it is oxidised to give 2, 4-dinitrophenol (main product) and 2, 6-dinitrophenol (small amount).

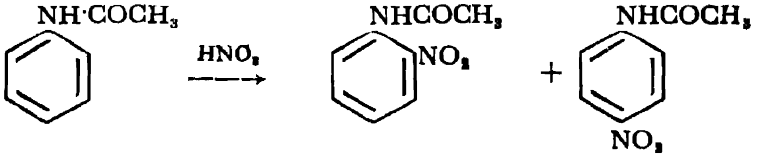


m-dinitrobenzene 2, 4-dinitrophenol 2, 6-dinitrophenol

It is used in the manufacture of explosives, *m*-phenylenediamine and dyestuffs.

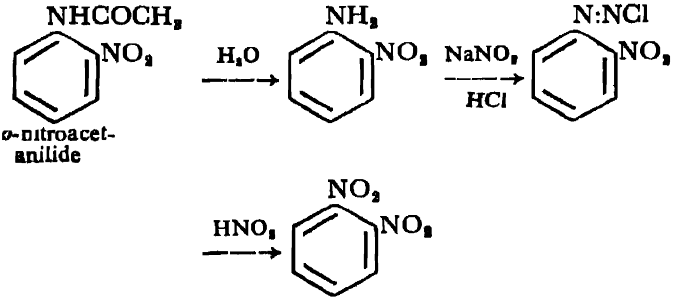
5. Ortho- and Para-Dinitrobenzenes, $C_6H_4(NO_2)_2$.—*o*-Dinitrobenzene is isolated from the mother liquor left after removing the crystals of *m*-isomer from the mixture of *m*- and *o*-isomers obtained on nitration of nitrobenzene.

In another method acetanilide is nitrated to get *o*- and *p*-nitroacetanilide.



Acetanilide Ortho- Para-
nitroacetanilides

The isomers are separated and deacetylated to get *o*- and *p*-nitroanilines. These are diazotised in presence of cuprous oxide to get *o*- and *p*- dinitrobenzenes.



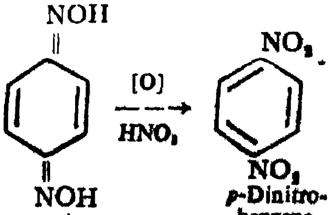
o-nitroacetanilide

o-Dinitrobenzene

During the nitration of amino and hydroxy compounds it is necessary to protect the —NH_2 or —OH group in the ring before nitration since these compounds are very easily oxidised by nitric acid. The —NH_2 is protected by acetylation.

Similarly, starting with *p*-nitroacetanilide we get *p*-dinitrobenzene.

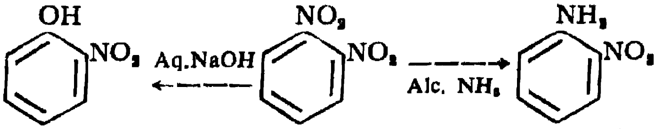
p-Dinitrobenzene may also be prepared by oxidation of *p*-benzoquinonedioxime with nitric acid.



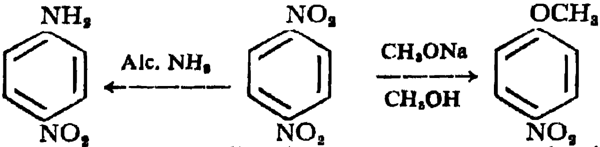
p-Benzoquinone-dioxime *p*-Dinitrobenzene

Both *o*- and *p*-dinitrobenzenes are colourless solids with m.p. 391K and 446K respectively. They resemble the *m*-isomer in their behaviour on reduction.

The two nitro groups are not rigidly attached to the nucleus as in the case of *m*-dinitrobenzene. One of these groups is readily replaced by $—NH_2$, $—OH$ or $—OCH_3$ group.



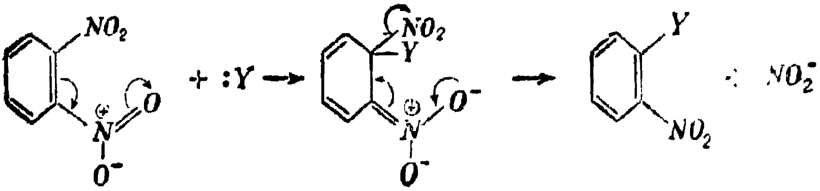
o-nitrophenol *o*-dinitrobenzene *o*-nitroaniline



p-nitroaniline *p*-dinitrobenzene *p*-nitromethoxybenzene

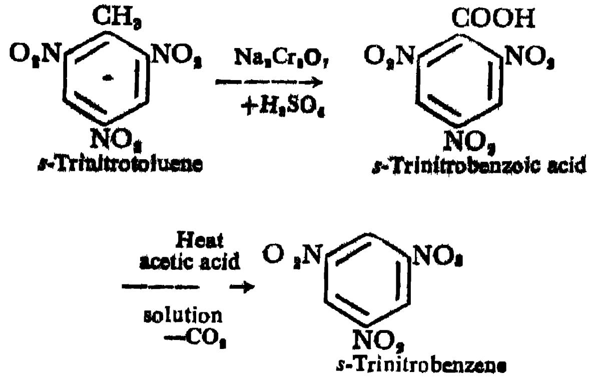
These reactions are characteristic of polynitro compounds having two nitro groups in *o*- and *p*-positions.

The mechanism of these reactions may be formulated as ws : $(Y = \overset{-}{O}H, NH_3, \overset{-}{O}Me)$:



6. *s*-Trinitrobenzene or 1, 3, 5-Trinitrobenzene, $C_6H_3(NO_2)_3$. —*s*-Trinitrobenzene may be prepared by nitration of *m*-dinitrobenzene with a mixture of fuming nitric acid and fuming sulphuric acid. The reaction is difficult and takes about 5 days to complete.

A better and convenient method for the preparation of *s*-trinitroenzene is by oxidising *s*-trinitrotoluene to trinitrobenzoic acid which on decarboxylation gives trinitrobenzene.

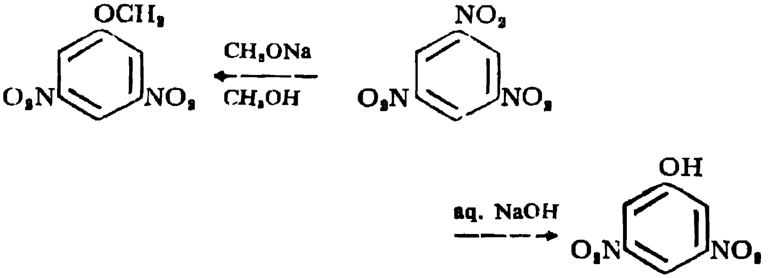


s-Trinitrotoluene

s-Trinitrobenzoic acid

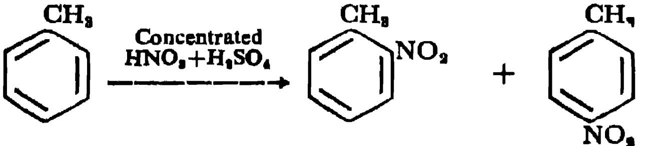
s-Trinitrobenzene

It is a colourless solid (m.p. 395K). It gives well-defined addition compounds with aromatic hydrocarbons, phenols, etc. One of the three nitro groups can be replaced by $—NH_2$, $—OH$ or $—OCH_3$ group as in the case of *o*- and *p*-dinitrobenzene.



It has a greater explosive power than *s*-trinitrotoluene and is used in making explosives.

7. **Nitrotoluenes, $C_6H_4(CH_3)NO_2$.**—Toluene is more readily nitrated than benzene due to the activating effect of the methyl group. When treated with concentrated nitric and sulphuric acids mixture, toluene gives a mixture of *o*- and *p*-nitrotoluenes.



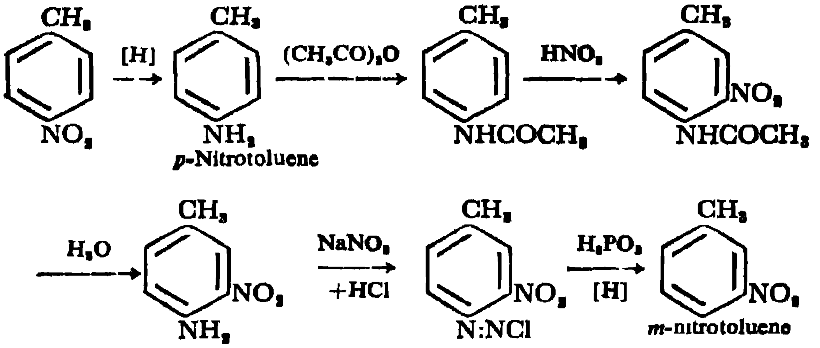
Toluene

o-Nitrotoluene (63-75%)

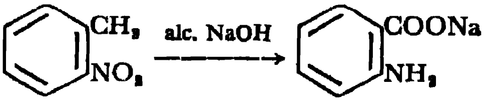
p-nitrotoluene (30%)

With acetyl nitrate the *o*-isomer (m.p. 269K ; b.p. 495K) is obtained in a larger yield (85-90%). It can be separated from the *p*-isomer (m.p. 327K ; b.p. 511K) by fractional distillation under reduced pressure. *m*-Nitrotoluene (m.p. 289K ; b.p. 500K) is obtained

by an indirect method. Starting with *p*-nitrotoluene different steps involved are :



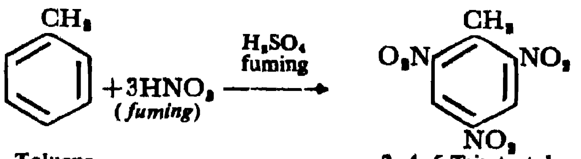
The three isomers on reduction form the corresponding toluidines while on oxidation corresponding nitrobenzoic acids are obtained. *o* Nitrotoluene on heating with ethanolic sodium hydroxide gives *o*-aminobenzoic acid.



It is an interesting example of the oxidising effect of nitro-group in the internal oxidation of *o*-nitrotoluene.

These are used in the manufacture of dyes and explosives. The *o*-isomer is used as a perfume.

8. **Trinitrotoluene (TNT).**—It is prepared by nitrating toluene with fuming nitric acid and fuming sulphuric acid mixture.



Toluene

2, 4, 6-Trinitrotoluene
or *s*-Trinitrotoluene

It is a pale-yellow crystalline solid (m.p. 354K). It is used as an explosive in shells, bombs and torpedoes. When mixed with ammonium nitrate, it forms the explosive *amatol*.

9. **TNT as High Explosive.**—*Explosives are compounds or mixtures which decompose producing large volumes of gases.* Explosion occurs in one of the three ways ; (*i*) by ignition ; (*ii*) by a slight shock ; (*iii*) by a severe shock. The requisites of a good explosive to be used inside an artillery shell are ;

(*i*) It should be able to withstand shock of the propellant which starts it on its course.

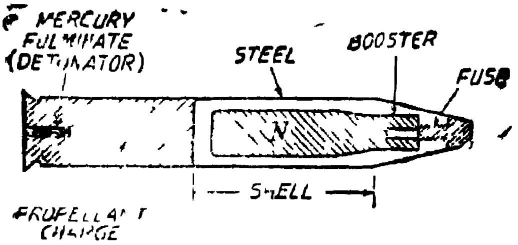
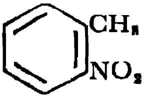


Fig. 39·3—Cross-section of an artillery shell for a 75 mm. field gun.

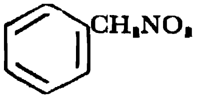
(*ii*) On reaching the target, it should be capable of exploding with great force.

TNT possesses these qualities and is used as shell-filler. The cross-section of an artillery shell is shown in Fig 39·3. On firing, the detonator starts the explosion of the propellant charge (grains of nitro-cellulose) and the shell shoots with a great speed. As it strikes the target a train of events occurs within a fraction of a second. First the firing pin in the fuse head explodes a sensitive cap. This explodes the booster (a sensitive explosive). Finally, the main charge of the shell-filler (TNT) explodes and exerts a tremendous force.

10. Phenylnitromethane, $C_6H_5CH_2NO_2$.—It is isomeric with nitrotoluenes but has the nitro group present in the side-chain, not attached to the nucleus as in nitrotoluenes.

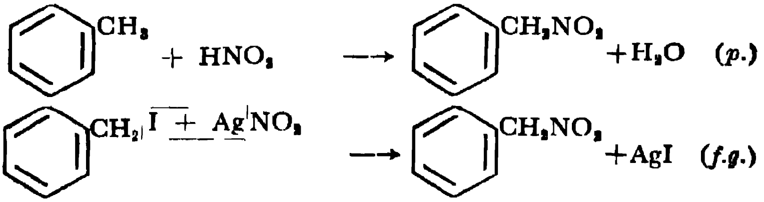


o-Nitrotoluene (NO_2 group attached to the nucleus)

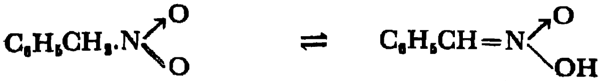


Phenylnitromethane (NO_2 group present in the side-chain)

It may be prepared by heating toluene with dilute nitric acid at 370K in a sealed tube or by heating benzyl iodide with aqueous alcoholic silver nitrite.



Phenylnitromethane behaves like a true primary aliphatic nitro-compound and exhibits tautomerism.



$$C_6H_5CH_2.N\begin{matrix}\nearrow O\\ \searrow O\end{matrix} \rightleftharpoons C_6H_5CH{=}N\begin{matrix}\nearrow O\\ \searrow OH\end{matrix}$$

Nitro form (yellow oil, b.p. 499K)

*Aci*nitro form (solid, m.p. 357K)

Both these forms have been isolated.

QUESTIONS

Essay Type :

1. Outline the preparation of nitrobenzene in the laboratory and in industry. Suggest methods for preparing (*a*) aniline, (*b*) hydrazobenzene,

(c) aminophenol, (d) m-dinitrobenzene and (e) m-nitroaniline from nitrobenzene. What is the specific test for the nitro group ? ***(Kerala B.Sc. 1973)***

2. Write a detailed note on the reduction products of nitrobenzene obtained by using various reducing agents.
(Delhi B.Sc. Hons. 1976 ; Rajasthan 1972)

3. Discuss the different methods for the preparation of aromatic nitro compounds. Discuss their industrial importance.

4. Describe the method of preparation and important properties of (a) meta-nitrotoluene, (b) m-dinitrobenzene, and (c) phenylnitromethane.

Short Answer Type :

1. Give the mechanism of nitration of benzene with conc. HNO_3 and conc. H_2SO_4. *(Delhi B.Sc. Hons. 1977, 76)*

2. What is nitration ?

3. On what factors does the number of nitro groups introduced during nitration of a compound depend ?

4. How will you prepare *o*- and *p*-dinitrobenzenes ?

5. How do you explain the ease of substitution of one nitro group in *o* dinitrobenzene by nucleophile ?

6. What is an explosive ? How does an explosion occur ?

7. Write equations for the reactions between :

(1) Benzene+ (*i*) concentrated nitric and sulphuric acids mixture ; (*ii*) fuming nitric and sulphuric acids mixture

(2) Toluene+(*i*) conc. nitric and sulphuric acids mixture ; (*ii*) fuming nitric and sulphuric acids mixture ; (*iii*) Acetyl nitrate.

(3) Phenol + (*i*) dilute nitric acid ; (*ii*) concentrated nitric acid.

(4) Sulphonation, chlorination and further nitration of nitrobenzene.

(5) *m*-Dinitrobenzene+ (*i*) sodium sulphide ; (*ii*) metal+acid ; (*iii*) alkaline $K_3Fe(CN)_6$.

(6) *o*-Nitrotoluene heated with alcoholic NaOH.

(7) 2, 4, 6-trinitrotoluene+ (*i*) aq.NaOH ; (*ii*) alc NH_3 ; (*iii*) methanolic CH_3ONa.

8. What happens when *o*- or *p*-Dinitrobenzene is boiled with (*i*) aqueous caustic soda ; (*ii*) alcoholic ammonia ; (*iii*) methanolic sodium methoxide.

9. How will you bring about the following conversions :

(*i*) *p*-nitrotoluene into *m*-nitrotoluene ; (*ii*) *o*-nitro-acetanilide into *o* dinitrobenzene ; (*iii*) 2, 4, 6-trinitrotoluene into *s*-trinitrobenzene.

10. Give the structure of products when nitrobenzene reacts with the following :

(*i*) Zn+dil HCl ; (*ii*) $Zn+NH_4Cl$; (*iii*) $LiAlH_4$.
(Osmania B.Sc. 1980)

11. Discuss the reduction of nitrobenzene in neutral and alkaline media.
(Delhi B Sc 1981

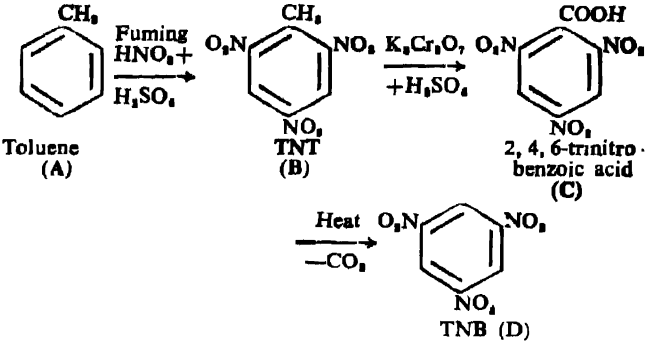
Problems :

1. An organic compound C_7H_8 (A) on treatment with fuming nitric acid and fuming sulphuric acid at 370K gives $C_7H_5O_6N_3$ (B). On treatment with acidified $K_2Cr_2O_7$ (B) gives $C_7H_3O_8N_3$ (C) which when heated in acetic acid solution yields $C_6H_3O_6N_3$ (D). Identify the compounds A to D.

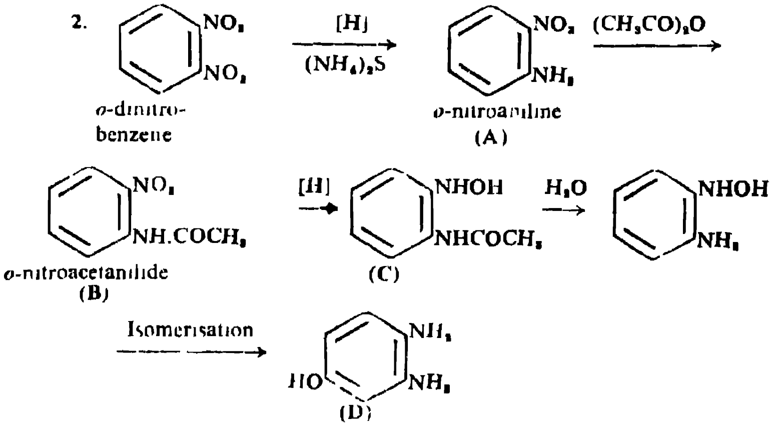
2. On reduction with $(NH_4)_2S$ *o*-dinitrobenzene gives $C_6H_6O_2N_2$ (A) which on treatment with acetic anhydride gives $C_8H_8O_3N_2$ (B). This on reduction forms $C_8H_{10}ON_2$ (C) which is hydrolysed by a mineral acid and the product of hydrolysis isomerises to $C_8H_8ON_2$ (D). Identify the compounds A to D.

ANSWERS

1.


CH₃
Fuming HNO₃+
H₂SO₄
O₂N
CH₃
NO₂
NO₂
K₂Cr₂O₇
+H₂SO₄
COOH
O₂N
NO₂
NO₂
Toluene
(A)
TNT
(B)
2, 4, 6-trinitro-benzoic acid
(C)
Heat
—CO₂
O₂N
NO₂
NO₂
TNB (D)

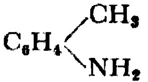
2.


NO₂
NO₂
o-dinitro-benzene
[H]
(NH₄)₂S
NO₂
NH₂
o-nitroaniline
(A)
(CH₃CO)₂O
NO₂
NH.COCH₃
o-nitroacetanilide
(B)
[H]
NHOH
NHCOCH₃
(C)
H₂O
NHOH
NH₂
Isomerisation
NH₂
NH₂
HO
(D)

40

Aromatic Amino-Compounds

1. Amino-compounds or Aromatic Amines.—In the case of aromatic compounds, the amino group may be attached to the nucleus or it may be present in the side-chain. *Those having the amino group attached to a nuclear carbon atom are called* **Amino-compounds** or aromatic amines, *e.g.*, aniline, $C_6H_5NH_2$. Like aliphatic amines, aromatic amino-compounds, derivatives of ammonia as they are, may be primary, secondary or tertiary according as one, two or all the hydrogen atoms of ammonia are replaced by aryl radicals.

$C_6H_5NH_2$	 $C_6H_4\begin{cases}CH_3\\NH_2\end{cases}$	$(C_6H_5)_2NH$;	$(C_6H_5)_3N$
Phenylamine or Benzenamine *or* aniline (*Primary*)	Methylbenzenamine or toluidine (*Primary*)	Diphenylamine (*Secondary*)	Triphenylamine (*Tertiary*)

In case of secondary and tertiary amino-compounds, all the hydrogen atoms of ammonia may not be replaced by aryl groups. There may be both aryl and alkyl groups. Such amines are termed *mixed*, *e.g.*,

$C_6H_5NH.CH_3$	$C_6H_5N(CH_3)_2$
N-Methylaniline (*Mixed* ; *Secondary*)	*N*, *N*-Dimethylaniline (*Mixed* ; *Tertiary*)

The basic character of an amino-compound decreases as the number of aryl groups increases, *e.g.*, aniline. $C_6H_5NH_2$ is a weaker base than ammonia, diphenylamine, $(C_6H_5)_2NH$ is weaker still while triphenylamine, $(C_6H_5)_3N$ is not at all basic. Purely aromatic quaternary compounds of the type $(C_6H_5)_4NX$, are unknown. Compounds of the type $[(C_6H_5)_3\overset{+}{N}R]\overset{-}{X}$ are, however, known. Compounds containing two amino-groups are called **diamines**, *e.g.*, phenylenediamine or benzenediamine, $C_6H_4(NH_2)_2$.

Aromatic compounds with **amino-group** *present in the side-chain are called* **Araliphatic amines,** *e.g.*, benzylamine, $C_6H_5CH_2NH_2$. In these hydrogen atom of the alkyl group has been replaced by an aryl group. They behave very much like the aliphatic amines.

PRIMARY AMINO-COMPOUNDS

2. General Methods of Preparation of Primary Amino-compounds.

(1) *By reduction of Nitro-compounds.* Various reducing agents which may be used are tin, iron or zinc with hydrochloric acid.

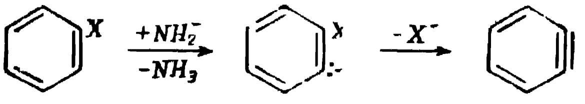
$$ArNO_2 + 6[H] \xrightarrow[+acid]{Metal} ArNH_2 + 2H_2O \qquad (v.g.\text{-}ex.)$$

(2) ***Ammonolysis of halogeno-compounds*** with liquid ammonia under pressure and high temperature in the presence of catalyst (Cu_2O).

$$2C_6H_5Cl + 2NH_3 + Cu_2O \xrightarrow{470K} 2C_6H_5NH_2 + 2CuCl + H_2O \qquad (90\%)$$

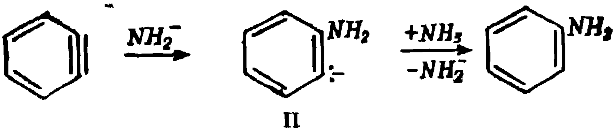
This is not a simple displacement as it appears to be. The reaction involves two stages : *elimination* and then *addition*. The intermediate molecule is termed *benzyne*.

(*i*) Elimination stage involves two steps : abstraction of a hydrogen atom (step 1) by the amide ion to form NH_3 and carbanion I which then loses halide ion (step 2) to from benzyne.



I

(*ii*) The addition stage involves two steps : attachment of the amide ion (step 3) to form carbanion II, which then reacts with an acid, NH_3, to abstract H^+ (step 4).



II

It may be that the addition involves a single step. If this is so, the transition state is probably one in which the attachment of nitrogen has proceeded to a greater extent than attachment of hydrogen and it has, therefore, considerable carbanion character.

In benzyne an additional weak bond is formed between two carbon atoms by sideway overlap of sp^2 orbitals (Fig. 40·1). The new bond orbital lies on the side of the ring, and has little interaction with the π cloud above and below the ring.

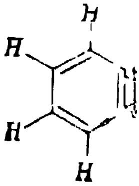
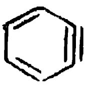
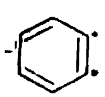


Fig. 40·1—Benzyne molecule.

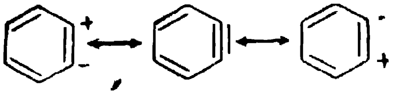
Structure of Benzyne. It is still uncertain. Three possible structures of benzyne are :



I
Benzyne



II
Diradical



III
Dipolar ion

If structure I is accepted, benzyne would be a distorted acetylene and should, therefore, be unstable. Structure II is also unlikely because benzyne shows little resemblance to a diradical in its chemical behaviour. In structure III benzyne is represented as a dipolar ion. On the basis of this structure we can explain the attack by nucleophiles like NH_2^-. Because of this uncertainty of structure some people prefer to name it as, *1,2-dehydrobenzene* (non-committal name in place of benzyne which implies the presence of a triple bond.

(3) ***Ammonolysis of phenols*** with ammonia in presence of $ZnCl_2$ at 570K.

$$\underset{\text{Phenol}}{C_6H_5OH} + NH_3 \xrightarrow[570K]{ZnCl_2} \underset{\text{Aniline}}{C_6H_5NH_2} + H_2O$$

(4) *By reduction of nitroso-compounds* with tin and hydrochloric acid.

$$\underset{\text{Nitrosobenzene}}{C_6H_5NO} + 4[H] \longrightarrow \underset{\text{Aniline}}{C_6H_5NH_2} + H_2O$$

(5) *Hofmann's hypobromite method.* By the action of bromine and alkali on amides (*For mechanism see Chapter 25*).

$$\underset{\text{Benzamide}}{C_6H_5CONH_2} \xrightarrow{Br_2/KOH} \underset{\text{Aniline}}{C_6H_5NH_2}$$

(6) *Through reductive amination of aldehyde and ketones.* Aldehydes and ketones can be converted into primary amines by their catalytic or chemical reduction in the presence of ammonia. The process is termed reductive amination which proceeds with the formation of an imine as an intermediate product

$$\underset{\text{Benzaldehyde}}{C_6H_5CH{=}O} + NH_3 \overset{-H_2O}{\rightleftharpoons} \underset{\text{Imine}}{C_6H_5CH{=}NH} \xrightarrow[\substack{90\text{ atm}\\ 310\text{-}340K}]{H_2/Ni} \underset{\text{Benzylamine}}{C_6H_5CH_2NH_2}$$

Secondary amines are obtained on using a primary amine in place of ammonia.

$$\begin{array}{l} C_6H_5CH{=}O + H_2NC_2H_5 \overset{-H_2O}{\rightleftharpoons} C_6H_5CH{=}NC_2H_5 \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \big\downarrow {}^{*}LiBH_3CN/CH_3OH \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \underset{\substack{\text{Benzylethylamine}\\ (\textit{a secondary amine})}}{C_6H_5CH_2NHC_2H_5} \end{array}$$

3. **Aniline (Benzenamine), $C_6H_5NH_2$.**—Aniline was first prepared by Unverdorben (1826) who obtained it by distilling indigo and was named aniline by Fritzsche in 1814 after *anil*, the Portuguese word for indigo.

Preparation : (*a*) **Laboratory Method.** In the laboratory aniline is prepared by the reduction of nitrobenzene with tin and hydrochloric acid.

$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} + 6[H] \longrightarrow \underset{\text{Aniline}}{C_6H_5NH_2} + 2H_2O \qquad (80\%)$$

Expt. Nitrobenzene (20 g) and granulated tin (40 g) are taken in a round-bottom flask fitted with a reflux condenser. To this is added conc. hydrochloric acid (100 cm³) in small amounts (10 cm³ at a time). The flask is shaken after each addition and the temperature not allowed to rise above 360K. Towards the end, the reaction is slow and larger bulks of acid can be added at a time. The flask is heated on a water bath until the smell of nitrobenzene disappears. On cooling a solid mass of the formula $(C_6H_5NH_2.HCl)_2SnCl_4$ separates out.

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* A reducing agent similar to $LiBH_4$. It reduces iminium group more rapidly than it reduces carbonyl group.

$$Sn + 4HCl \longrightarrow SnCl_4 + 4H$$

$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} + 6[H] \longrightarrow \underset{\text{Aniline}}{C_6H_5NH_2} + 2H_2O$$

$$\underset{\text{Aniline}}{2C_6H_5NH_2} + 2HCl + \underset{\substack{\text{Stannic}\\\text{chloride}}}{SnCl_4} \longrightarrow \underset{\substack{\text{Double salt}\\\textit{(A solid mass)}}}{(C_6H_5NH_2.HCl)_2SnCl_4}$$

The solid mass is treated with a concentrated caustic soda solution until the solution is clear and alkaline. Aniline is liberated and floats as a dark brown oil.

$$\underset{\text{Solid mass}}{(C_6H_5NH_2.HCl)_2SnCl_4} + 8NaOH \longrightarrow \underset{\substack{\text{Aniline}\\\textit{(Oily layer)}}}{2C_6H_5NH_2} + \underset{\substack{\text{Sod. stannate}\\\textit{(Soluble)}}}{Na_2SnO_3} + 6NaCl + 5H_2O$$

Aniline is recovered from the above mixture by steam distillation. The distillation is continued until the distillate is no longer turbid. To the distillate is added common salt when practically whole of aniline separates. It is extracted with ether in small lots. The ethereal extract is dried over solid caustic potash (calcium chloride forms an addition compound with aniline) and ether removed from it by distillation over water bath. Aniline so obtained is purified by redistillation.

(*b*) **Commercial Preparation.** Aniline is prepared on a commercial scale :

(*i*) *By the reduction of nitrobenzene with scrap iron and concentrated hydrochloric acid.*

$$Fe + 2HCl \longrightarrow FeCl_2 + 2[H]$$

$$C_6H_5NO_2 + 6[H] \longrightarrow C_6H_5NH_2 + 2H_2O$$

Here not only the costly tin is replaced by cheaper iron but also there is a saving of hydrochloric acid as the acid is regenerated by hydrolysis of ferrous chloride.

$$FeCl_2 + 2H_2O \longrightarrow Fe(OH)_2 + 2HCl$$

$$C_6H_5NO_2 + 6Fe(OH)_2 + 4H_2O \longrightarrow C_6H_5NH_2 + 6Fe(OH)_3$$

Thus only 1/40th of the theoretical amount of hydrochloric acid is actually used.

Concentrated hydrochloric acid, water and scrap iron are placed in the reducing pan (*Reducer*—Fig. 40·2). Steam is blown into the reducer and nitrobenzene run in a fine stream. The contents are kept in agitation by a stirrer fitted in the reducing pan. No further heating is necessary as the heat of reaction is enough to complete the reduction.

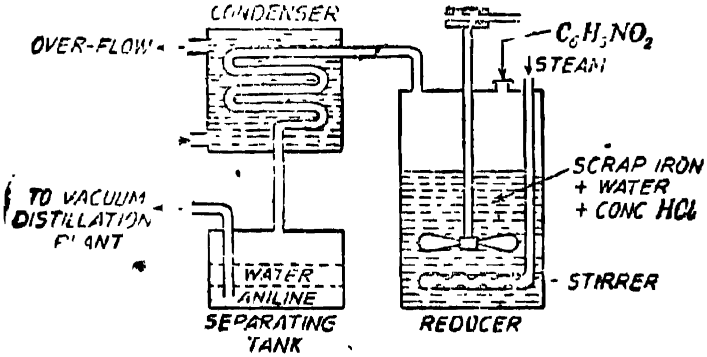


Fig. 40·2—Manufacture of aniline.

At the end milk of lime is added to neutralize the acid and to decompose aniline hydrochloride ($C_6H_5NH_2.HCl$) formed and aniline set free is separated by distillation in steam. The distillate is collected wherein crude aniline forms the lower layer. Crude aniline is taken to a vacuum distillation plant and distilled under reduced pressure when pure aniline distils over.

(*ii*) *By the catalytic reduction of nitrobenzene.* Aniline may also be manufactured by catalytic reduction of nitrobenzene using nickel catalyst.

(*iii*) *By the action of ammonia on chlorobenzene.* Chlorobenzene reacts with excess of aqueous ammonia when heated at 470K under pressure in the presence of cuprous oxide.

The latter decomposes the ammonium chloride formed in the reaction and thus renders the reaction irreversible.

$$\underset{\text{Chlorobenzene}}{2C_6H_5Cl} + 2NH_3 + Cu_2O \xrightarrow[\text{Pressure}]{470K} \underset{\text{Aniline}}{2C_6H_5NH_2} + 2CuCl + H_2O \quad (90\%)$$

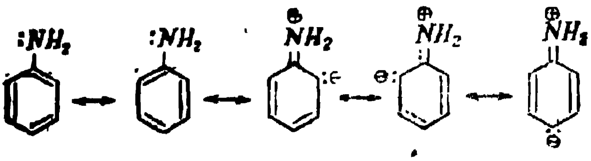
Properties : Physical. When freshly prepared, aniline is a colourless oily liquid (b.p. 457K) with an unpleasant odour and is poisonous in nature. Being sensitive to oxidation, colour rapidly chages to dark brown when exposed to air. It is practically insoluble in water but readily soluble in organic solvents.

Chemical. The molecule of aniline, $C_6H_5NH_2$ is made up of (*i*) an amino-group attached to the nuclear carbon, and (*ii*) the benzene nucleus. Its reactions are the reactions of these two groups :

(*a*) *Reactions of the Amino-group.*

(1) **Basic Nature.** Aniline is weakly basic and gives salts with acids, *e.g.*, $C_6H_5NH_2.HCl$, aniline hydrochloride with hydrochloric acid, $(C_6H_5NH_2)_2H_2SO_4$, aniline sulphate with sulphuric acid and double salts with platinum chloride ($PtCl_4$) and gold chloride ($AuCl_3$) *e.g.*, $(C_6H_5NH_2.HCl)_2.PtCl_4$.

Aniline is a weaker base than the primary aliphatic amines due to resonance which is not possible in aliphatic amines.



Owing to resonance, the lone pair of electrons on the nitrogen atom is less available for coordinating with a proton. In addition to this, the small positive charge on the nitrogen atom tends to repel the proton.

Aniline may accept a proton to give a small concentration of the cation $C_6H_5\overset{+}{N}H_3$ (anilinium) which does not show resonance.

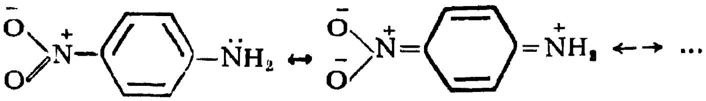
Since there are more resonating structures possible for aniline than for the anilinium ion, the former will be stabilised with respect to the latter.

The increased electron density on the ring accounts for the ease of substitution and for ortho- and para-orientation.

Effect of Ring substitution on Basicity. The effect of ring substituent, G depends on the following :

(*i*) ***Nature of G whether it is electron-attracting or electron-releasing.*** An electron-releasing group reduces the resonance of NH_2 group with the ring and, therefore, increases the basicity. The electron-withdrawing group (—I effect) tends to draw the electron pair of the N atom of $\ddot{N}H_2$ group into the ring and consequently decreases the basicity.

(*ii*) ***Its ability to enter into resonance with amino group.*** Groups like nitro having strong —R effect decrease the basicity and others like methoxy having a strong +R effect increase the basicity.



(*iii*) ***Its Position.*** The electron-withdrawing or electron-releasing effect is more at *o*- and *p*-positions than at the *m*-. There may be added complications due to steric effect.

Basicity of various substituted anilines are given below in terms of their pK_a values. Higher the pK_a value of a compound, greater its basicity. For aniline, pK_a=4·58.

Substituent in $C_6H_5NH_2$	pK_a		
	o-	*m*-	*p*-
CH_3	4·39	4·69	5·12
NO_2	0·29	2·50	1·02
Cl	2·64	3·34	3·98
CH_3O	4·49	4·20	5·29
NH_2	4·47	4·[illegible]8	6·08

Effect of various substituents on the basicity of aniline as seen from the pK_a values given in the above table can be explained as follows :

(*i*) **CH_3.** It has a +I effect and, therefore, increases the basicity from pK_a=4·58 to 4·69 (for *m*-) and 5·12 (for *p*-). The effect is more when CH_3 is in *p*-position than in *m*-position as explained earlier.

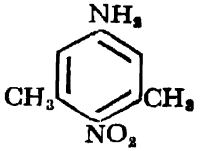
(*ii*) **NO_2.** It exerts —R as well as —I effects and, therefore, decreases the basicity as seen from a decrease in pK_a values. The effect in *o*- and *p*- position is much more than in *m*-position. This is because from *m*-position it cannot exert —R effect. Decrease in basicity is only due to —I effect.

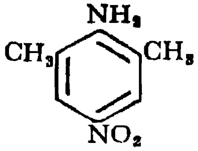
Halogens exert both +R and —I effect but +R effect is very small. Presence of halogens decreases the basicity of $:NH_2$ group due to —I effect.

Methoxy and Amino groups. The *p*-OMe group has a +R effect and the basicity increases due to its presence. In the *m*-position it exerts only a −I effect and this decreases the basicity. Effect of amino group can be explained similarly.

It is evident from the above discussion that when the substituent group can enter into resonance with the rest of the molecule, it exerts a marked effect on its basicity. For resonance the resonating structures must be planar or nearly planar. If the planarity is partially reduced or completely prevented due so some steric effect, the resonance is diminished or completely prevented. This is called steric inhibition of resonance.

3, 5- dimethyl-4-nitroaniline is a stronger base than 2, 6-dimethyl-4-nitroaniline on account of steric inhibition. In the first





pK_a 2·49 0·95

case, the nitro group cannot enter into resonance with the amino-group and is not able to reduce the basicity appreciably. In the second case it can enter into resonance and, therefore, reduces the basicity appreciably.

N-**Alkylated anilines.** *These are stronger bases than aniline.* *N*-ethylaniline is a stronger base than *N*-methylaniline. This cannot be explained on the basis of +I effect of alkyl groups resulting in increased resonance of the lone pair with the ring, since that would make *N*-alkylanilines weaker bases than aniline. It is considered as due to the steric effect, which inhibits resonance of the lone pair on nitrogen and makes it more available for protonation. Ethyl group being bigger than methyl has more steric effect, so *N*-ethyl aniline is stronger base than *N*-methylaniline. pK_a values of some of these are given for reference.

Base	$PhNH_2$	PhNHMe	PhNHEt	$PhNMe_2$	$PhNEt_2$
pK_a	4·58	4·85	5·11	5·06	6·56

(2) **Acylation.** With an acid chloride or an acid anhydride, H-atom of the amino-group is replaced by acyl group to give an anilide.

$$C_6H_5NH_2 + \underset{\text{Acetyl chloride}}{CH_3COCl} \longrightarrow \underset{\text{Acetanilide}}{C_6H_5NH.COCH_3} + HCl$$

$$C_6H_5NH_2 + \underset{\text{Benzoyl chloride}}{C_6H_5COCl} \longrightarrow \underset{\text{Benzanilide}}{C_6H_5NH.COC_6H_5} + HCl$$

(3) **Alkylation.** When treated with alkyl halides, the hydrogen atoms of the amino-group are replaced by alkyl groups to give mixed, secondary and tertiary amino-compounds.

$$\underset{\text{Aniline}}{C_6H_5NH_2} \xrightarrow{CH_3I} \underset{N\text{-Methylaniline}}{C_6H_5NH.CH_3} \xrightarrow{CH_3I} \underset{N,N\text{-Dimethylaniline}}{C_6H_5N(CH_3)_2}$$

(4) **Carbylamine Reaction.** On heating aniline with chloroform and alcoholic potash, an obnoxious smell of carbylamine (an isocyanide) is noticed.

$$\underset{\text{Aniline}}{C_6H_5N\overline{H_2}} \overline{+ Cl_3}\underset{\text{Chloroform}}{HC} + \underset{\text{Alcoholic potash}}{3KOH} \rightarrow \underset{\text{Phenyl isocyanide}}{C_6H_5NC} + 3KCl + 3H_2O$$

The mechanism proposed for the reaction is as follows :

$$CHCl_3 + OH^- \rightleftharpoons :CCl_3^- + H_2O$$
$$:CCl_3^- \longrightarrow :CCl_2 + Cl^-$$

$$\underset{\text{Aniline}}{PhNH_2} \quad CCl_2 \longrightarrow Ph\overset{+}{N}H_2—\overset{-}{C}Cl_2 \xrightarrow{-H^+}$$

$$PhNH\overset{-}{C}Cl_2 \xrightarrow[-H^+]{-Cl^-} PhN=\overset{-}{C}Cl \xrightarrow{-Cl^-} \underset{\text{carbylaminobenzene}}{PhN \equiv C}$$

(5) **Action with Grignard Reagent.** Aniline reacts with Grignard reagent to form hydrocarbons.

$$RMgBr + C_6H_5NH_2 \longrightarrow RH + C_6H_5NH.MgBr$$

(6) **Diazotisation.** An ice-cold solution of aniline in hydrochloric acid when treated with an ice-cold solution of sodium nitrite gives benzenediazonium chloride, which decomposes on warming to give phenol.

$$NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$$

$$\underset{\text{Aniline}}{C_6H_5NH_2} + HCl + \underset{\text{Nitrous acid}}{HNO_2} \longrightarrow \underset{\text{Benzenediazonium chloride}}{C_6H_5N_2Cl} + 2H_2O$$

$$C_6H_5\underline{N_2Cl + H}OH \longrightarrow \underset{\text{Phenol}}{C_6H_5OH} + N_2 + HCl$$

(7) **Action with Carbonyl Chloride.** Aniline reacts with carbonyl chloride to give carbonylaminobenzene.

$$\underset{\text{Aniline}}{C_6H_5N\underline{H_2 + Cl_2}C=O} \longrightarrow \underset{\text{carbonylaminobenzene}}{C_6H_5N=C=O} + 2HCl$$

(8) **Condensation with Aldehydes.** Aniline gives condensation products (*Schiff bases*) with aromatic aldehydes.

$$\underset{\text{Aniline}}{C_6H_5N\underline{H_2 + O}}\underset{\text{Benzaldehyde}}{=HC.C_6H_5} \longrightarrow \underset{\text{Benzylideneaniline}}{C_6H_5N=HC.C_6H_5} + H_2O$$

The Schiff bases on hydrolysis easily give free amine. Their formation offers an easy method of protecting an amino-group before altration.

On reduction a Schiff base gives a secondary amino-compound.

$$\underset{\text{Schiff base}}{C_6H_5N{=}CH.Ar} \xrightarrow{H_2/Ni} \underset{\text{Secondary amino-compound}}{C_6H_5NH.CH_2Ar}$$

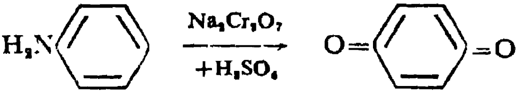
(9) **Action with Carbon Disulphide.** On heating with an alcoholic solution of carbon disulphide and solid KOH, it gives *s*-diphenylthiourea or thiocarbanilide (used in vulcanisation of rubber).

$$\underset{\text{Aniline (2 mol)}}{\left.\begin{array}{l}C_6H_5NH|\overline{H}\\ C_6H_5NH|\underline{H}\end{array}\right|}+S{=}C{=}S+2KOH\rightarrow\underset{\substack{s\text{-Diphenylthiourea}\\ \text{m.p. 427K}}}{(C_6H_5NH)_2CS}+K_2S+2H_2O$$

(10) **Oxidation.** The high electron density on the ring in the aniline molecule makes oxidation (*electron removal*) very easy. Thus it turns dark red on exposure to air due to oxidation More intense colours are given by stronger oxidising agents. For example,

Oxidising agent	**Colour produced**
Bleaching powder	Deep violet
$Na_2Cr_2O_7$+conc. H_2SO_4	Intense blue
$Na_2Cr_2O_7$+$CuSO_4$+dil. acid	Aniline black dye

Oxidation of aniline with sodium dichromate and sulphuric acid under carefully controlled conditions gives *p*-benzoquinone.



p-Benzoquinone

(11) **Action with Hypohalous Acids or Alkali Metals.** Hydrogen atoms of the amino-group are replaced by halogen atoms when aniline is treated with hypohalous acids, *e.g.*, with hypochlorous acid, HClO.

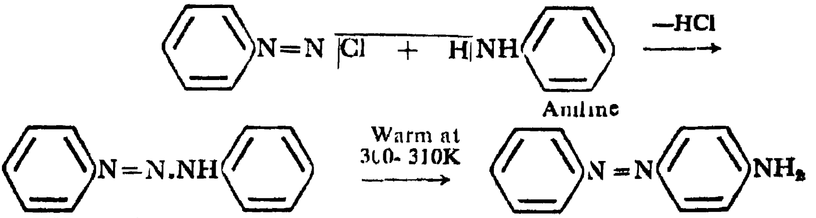
$$C_6H_5NH_2+2HClO\rightarrow C_6H_5NCl_2+2H_2O$$

When heated with sodium or potassium, the metal dissolves with the evolution of hydrogen.

$$2C_6H_5NH_2+2Na\rightarrow 2C_6H_5NH.Na+H_2$$

(*b*) *Reactions of the Benzene Nucleus.*

(1) **Coupling Reaction.** Aniline gives a reaction with diazonium salts yielding azo-dyes.



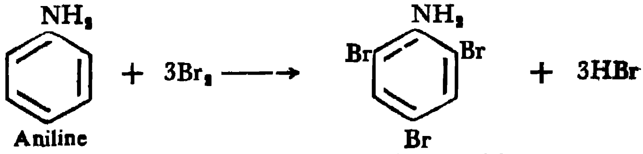
Aniline

Diazoaminobenzene
(*Yellow dye*)

or when left
in mother liquor

p-aminoazobenzene
(*brilliant orange-red dye*)

(2) **Halogenation.** Presence of amino-group in the nucleus facilitates halogenation. A symmetrical trisubstitution product is obtained on chlorination or bromination.

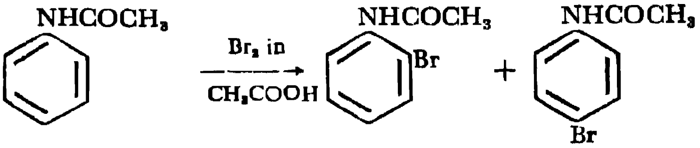


Aniline

2,4,6-tribromoaniline (*light yellow ppt.*)

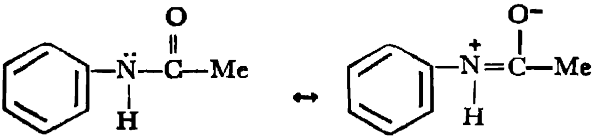
In chlorination, a water-free solvent such as chloroform should be used otherwise oxidation takes place.

Monochloro or monobromoaniline may be prepared by chlorination or bromination of acetanilide.



These on hydrolysis give the corresponding bromoanilines.

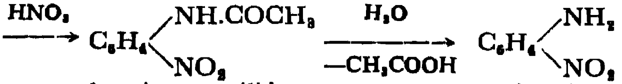
The deactivating effect of the acetyl group in acetanilide. It is considered to be due to the fact that the lone pair of the :NH$_2$ group enters into resonance with the carbonyl group and as a result of it the resonance with the ring decreases considerably.



From the resonance structure it is clear that *the availability of the lone pair for protonation decreases as a result of resonance. This explains the very weak basic character of acetanilide.*

(3) **Nitration.** Aniline being very susceptible to oxidation, direct nitration is not possible. The amino-group is protected by acetylating before nitration.

$$\underset{\text{Aniline}}{C_6H_5NH_2} + \underset{\text{Acetyl chloride}}{Cl.COCH_3} \xrightarrow{-HCl} \underset{\text{Acetanilide}}{C_6H_5NH.COCH_3}$$



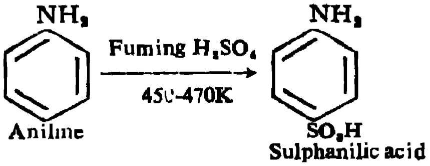
$$\xrightarrow{HNO_3} C_6H_4{\begin{smallmatrix}\nearrow NH.COCH_3\\ \searrow NO_2\end{smallmatrix}} \xrightarrow[-CH_3COOH]{H_2O} C_6H_4{\begin{smallmatrix}\nearrow NH_2\\ \searrow NO_2\end{smallmatrix}}$$

o- & *p*-nitroacetanilide *o*- & *p*-nitroaniline

The *p*-nitroaniline far exceeds the ortho-derivative in yield.

(4) **Sulphonation.** Aniline on heating with fuming sulphuric acid to 450-470K, gives *p*-aminobenzenesulphonic acid (*Sulphanilic*

acid). Why ? This is because sulphonation is known to be reversible and the *p*-isomer is known to be the most stable isomer.



Uses. Aniline is used : (*i*) For the manufacture of dyes.

(*ii*) For the preparation of certain synthetic drugs.

(*iii*) As an accelerator in vulcanizing rubber.

Test. (1) Gives carbylamine reaction (*see* page 2·556).

(2) To a solution of aniline in water add a little bleaching powder. A violet colour is produced which soon changes to brown and fades away.

(3) To a solution of aniline in sulphuric acid add potassium dichromate solution. A red colour slowly turning deep blue is obtained.

(4) Diazotise an ice-cold solution of aniline in hydrochloric acid with ice-cold sodium nitrite solution. Add a few drops of β-naphthol in excess of sodium hydroxide (*Coupling*). A brilliant-red dye is obtained.

(5) Treat with bromine water, a light yellow ppt of tribromoaniline is obtained.

4. Comparison of Aniline with Ethylamine.

(*a*) **Points of Similarity :**

(*i*) Basic nature.
(*ii*) Alkylation
(*iii*) Acylation.
(*iv*) Action of Sodium.
(*v*) Carbylamine reaction.
(*vi*) With HClO or Cl_2+NaOH.
(*vii*) With Grignard reagent.

(*b*) **Points of Difference :**

Ethylamine	Aniline
1. Colourless inflammable liquid (b p. 292K) with fishy ammoniacal odour.	1. Colourless oily liquid (b.p. 457K) with unpleasant odour.
2. Highly soluble in water, giving alkaline solution.	2. Practically insoluble in water.
3. With nitrous acid gives ethyl alcohol and nitrogen.	3. Gives diazonium salt in cold and phenol on heating.
4. Not easily oxidised.	4. Very susceptible to oxidation.
5. No substitution takes place in the ethyl radical.	5. Substitution in the benzene nucleus proceeds readily. It can be nitrated, sulphonated and halogenated.
6. Does not react with aldehydes.	6. Gives Schiff's base with aromatic aldehydes.
7. Does not give coupling reaction.	7. Gives coupling reaction.

5. Aniline Hydrochloride, $C_6H_5NH_2HCl$.—It is a colourless crystalline salt (m.p. 471K ; b.p. 518K) very soluble in water. It is precipitated by passing dry hydrogen chloride through a solution of aniline in ether, the yield is quantitative.

It is used in calico-printing. Aniline hydrochloride is made into a paste with potassium chlorate, copper sulphate and gum arabic. The cloth is printed with this paste and exposed to air when a black print is obtained due to oxidation of aniline to aniline black.

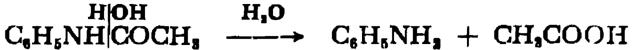
6. Acetanilide (*N*-phenylacetamide), $C_6H_5NHCOCH_3$.

Preparation. Acetanilide may be readily prepared, in very good yield, by heating aniline with acetyl chloride, acetic anhydride or glacial acetic acid. It is, however, usually prepared in the laboratory by the action of glacial acetic acid on aniline. Anhydroues zinc chloride is used as a dehydrating agent.

$$\underset{\text{Aniline}}{C_6H_5NH|\overline{H} + } \underset{\substack{\text{Acetic acid}\\ \text{(Glacial)}}}{\overline{HO}|COCH_3} \longrightarrow \underset{\text{Acetanilide}}{C_6H_5NH.COCH_3} + H_2O$$

The mixture of aniline (10 cm³), glacial acetic acid (12 cm³) and anhydrous zinc chloride (2 g) is gently boiled in a round-bottom flask provided with reflux condenser. The hot contents are poured into cold water with stirring when acetanilide crystals separate. These are removed, dried and recrystallized from boiling water or dilute alcohol.

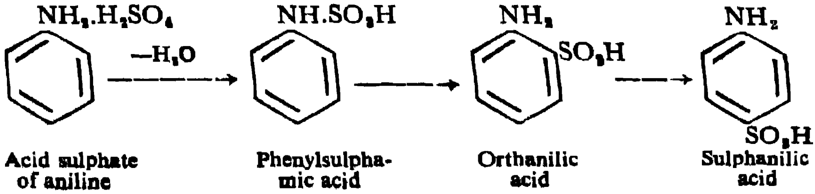
Properties. It is a colourless, crystalline (rhombic plates) substance (m.p. 387K), sparingly soluble in cold water but more soluble in hot water. On hydrolysis, *e.g.*, when heated with alkalis or mineral acids, it regenerates aniline and acetic acid.



$$\underset{\text{Acetanilide}}{C_6H_5NH\overset{H|OH}{|}COCH_3} \xrightarrow{H_2O} \underset{\text{Aniline}}{C_6H_5NH_2} + \underset{\text{Acetic acid}}{CH_3COOH}$$

Uses. It is used in medicine under the name of *Antifeberin*, for lowering body temperature and to relieve headache. It is a useful intermediate product in various reactions of aniline, *e.g.*, nitration wherein it is desirable to protect the amino-group.

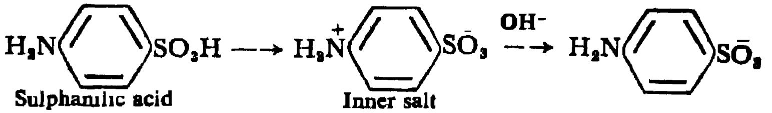
7. Sulphanilic acid (*p*-aminobenzenesulphonic acid), *p*-$NH_2.C_6H_4SO_3H$.—It is formed as the product when aniline is sulphonated with oleum at 450K. Some metanilic acid and a little orthanilic acid are also produced. It is, however, manufactured by the baking process—heating acid sulphate of aniline (from equal weights of aniline and conc. H_2SO_4) at 470K for some time. The reaction is believed to proceed as follows :



Acid sulphate of aniline — Phenylsulphamic acid — Orthanilic acid — Sulphanilic acid

Properties. It is an interesting compound as its properties are not those we expect of a compound containing an NH_2 group and a $—SO_3H$ group. Both aniline and benzenesulphonic acid have low m.p. but sulphanilic acid is a white solid which decomposes (at 550-570K) before melting. Sulphonic acids are generally very soluble in water but this is insoluble in organic solvents and nearly insoluble in water. It is soluble in aqueous bases but insoluble in aqueous acids.

These properties are understood from its dipolar ion (zwitter ion) character (structure I) a product of reaction between the acidic group and the basic group.



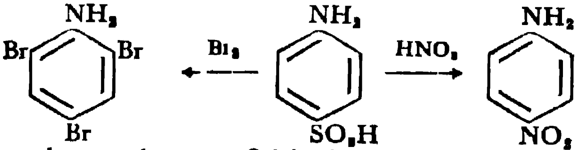
Sulphanilic acid

Inner salt
Zwitter ion
I
Insoluble in water

II
Soluble in water

High m.p. and insolubility in organic solvents are properties expected of any salt, and many salts are insoluble in water. In alkaline solution strongly basic OH^- ions pull H^+ ion away from the weakly basic $—NH_2$ group to yield *p*-amino-benzenesulphonate ion (II) which like most sodium salts is soluble in water. In acid solution structure I does not change and the compound, therefore, remains insoluble.

When treated with concentrated nitric acid, sulphonic group in sulphanilic acid is replaced by a nitro group to give *p*-nitroaniline. Similarly on bromination the sulphonic group is replaced by Br atom to give *s*-tribromoaniline.

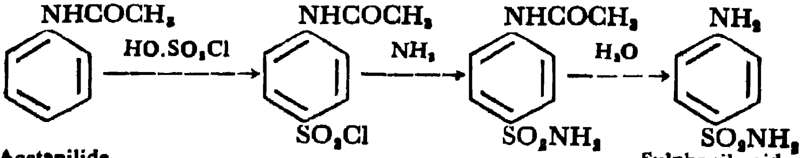


s-tribromoaniline Sulphanilic acid *p*-nitroaniline

It may be diazotised.

Uses. It is used in the manufacture of dyes and sulphanilamide drugs.

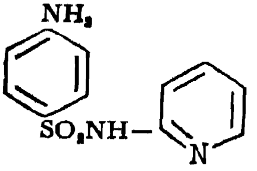
8. Sulphanilamide (*p*-aminobenzenesulphonamide).— Acetanilide is treated with chlorosulphonic acid and the product on reaction with ammonia followed by hydrolysis gives sulphanilamide.



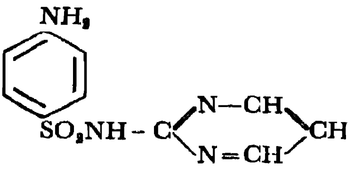
Acetanilide Sulphanilamide

It is a white crystalline solid (m.p. 439·5K). Importance of sulphanilamide lies in its use in the manufacture of sulpha drugs which have revolutionised the medical world. They have remarkable action in curing diseases like pneumonia, gonorrhoea, dysentery and bacterial infections in general.

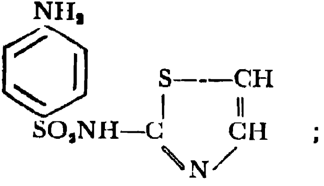
It will be interesting to note the structural formulae of some of our common sulpha drugs given below :



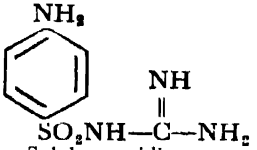
Sulphapyridine
(M. & B. 693)



Sulphadiazine

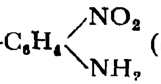


Sulphathiazole
(M. & B. 760-1942)



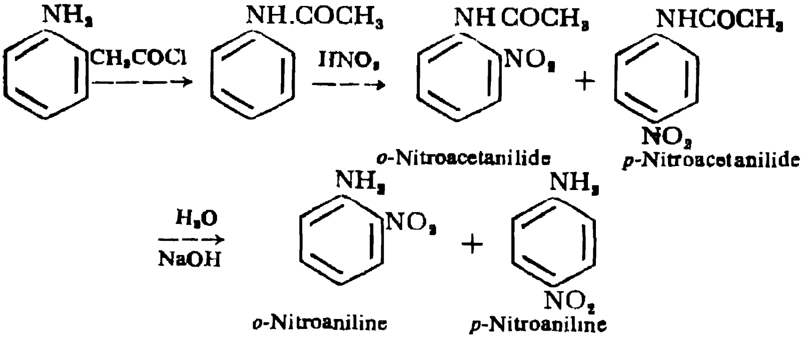
Sulphaguanidine
(1940)

9. **Nitroanilines.**—



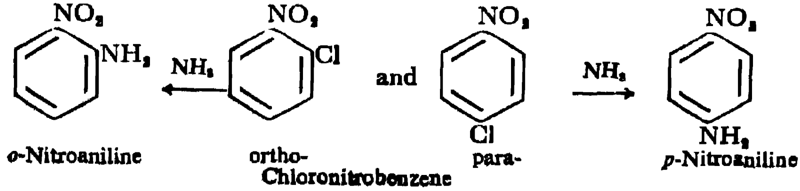
$C_6H_4\begin{cases} NO_2 \\ NH_2 \end{cases}$ (*o*-, *m*- and *p*-).

Preparation. *o*- and *p*-Nitroanilines are prepared by nitration of acetanilide followed by hydrolysis.

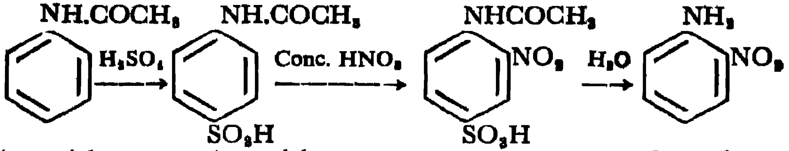


o-Nitroacetanilide (*solid*) is separated from *p*-Nitroacetanilide (*liquid*) by filtration and then hydrolysed with alkali.

o- and *p*-Nitroaniline may also be prepared by heating *o*- and *p*-chloronitrobenzenes with ammonia.

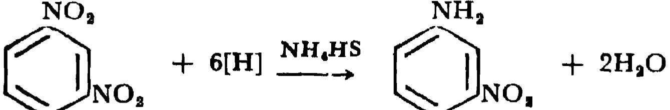


Nitration with acetyl nitrate gives exclusively the orth-product. The ortho-isomer is, however, usually prepared as under :



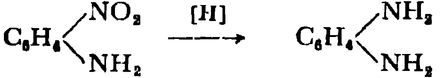
Acetanilide p-Acetanilide-sulphonic acid o-Nitroaniline

m-Nitroaniline is obtained by partial reduction of *m*-Dinitrobenzene with ammonium hydrogen sulphide or sodium sulphide.



Properties. All the three isomeric nitroanilines are solids (m.p. *o*=344K ; *m*=387K ; *p*=421K), sparingly soluble in water but readily soluble in alcohol.

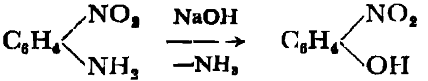
They are weaker bases than aniline. On reduction with metal and acid each one gives the corresponding phenylenediamine.



$$C_6H_4\left\langle\begin{matrix}NO_2\\NH_2\end{matrix}\right. \xrightarrow{[H]} C_6H_4\left\langle\begin{matrix}NH_2\\NH_2\end{matrix}\right.$$

o-, *m*- & *p*-nitroanilines *o*-, *m*- & *p*-phenylenediamine

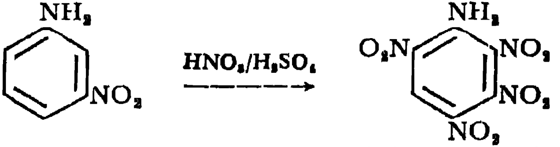
In *o*- and *p*-nitroanilines, the —NH_2 group is replaced by —OH on boiling with aqueous caustic soda solution (*cf.* chloronitrobenzenes, *page 2 513*)



$$C_6H_4\left\langle\begin{matrix}NO_2\\NH_2\end{matrix}\right. \xrightarrow[-NH_3]{NaOH} C_6H_4\left\langle\begin{matrix}NO_2\\OH\end{matrix}\right.$$

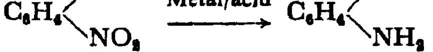
o- & *p*-nitroaniline *o*- & *p*-nitrophenol

m-Nitroaniline is not reacted upon by NaOH. On nitration with acid mixture it gives 2, 3, 4, 6-tetranitroaniline (TNA), an explosive.



m-nitroaniline 2, 3, 4, 6-tetra-nitroaniline

10. Toluidines (*o*-, *m*- & *p*-), **or, 2-, 3- & 4-Methylbenzenamines, $CH_3C_6H_4NH_2$.**—The three toluidines may be prepared by reduction of the corresponding nitrotoluenes.

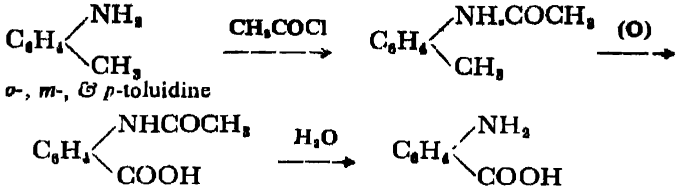


$$C_6H_4\left\langle\begin{matrix}CH_3\\NO_2\end{matrix}\right. \xrightarrow{\text{Metal/acid}} C_6H_4\left\langle\begin{matrix}CH_3\\NH_2\end{matrix}\right.$$

o-, *m*- & *p*-nitrotoluenes *o*-, *m*- & *p*-toluidines

Properties. *o*- & *m*- Toluidines are oily liquids (b.p. 474K and 473K respectively) while *p*-toluidine is a solid (m.p. 318K ; b.p. 473K). They are all insoluble in water, soluble in organic solvents and poisonous in nature.

They can be oxidised to the corresponding aminobenzoic acid after protecting the amino group.



$$C_6H_4\langle{}^{NH_2}_{CH_3} \xrightarrow{CH_3COCl} C_6H_4\langle{}^{NH.COCH_3}_{CH_3} \xrightarrow{(O)}$$

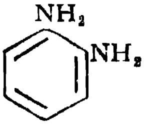
o-, m-, & p-toluidine

$$C_6H_4\langle{}^{NHCOCH_3}_{COOH} \xrightarrow{H_2O} C_6H_4\langle{}^{NH_2}_{COOH}$$

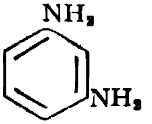
o-, m-, & p-aminobenzoic acid

They are all used in the manufacture of dyes.

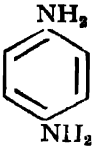
11. Benzenediamine or Phenylenediamines, $C_6H_4(NH_2)_2$. —Three benzenediamines are :



o-Phenylendiamine or 1, 2-Benzenediamine

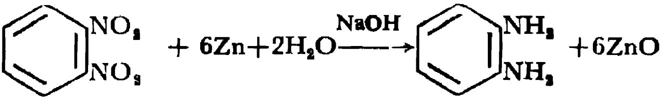


m-Phenylenediamine or 1, 3-Benzenediamine



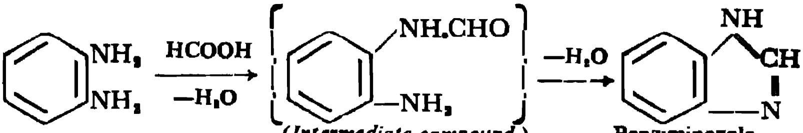
p-Phenylenediamine or 1, 4-Benzenediamine

o-**Phenylenediamine** (*1, 2-benzenediamine*). It is best prepared by the reduction of *o*-dinitrobenzene with zinc dust and aqueous alcoholic sodium hydroxide.



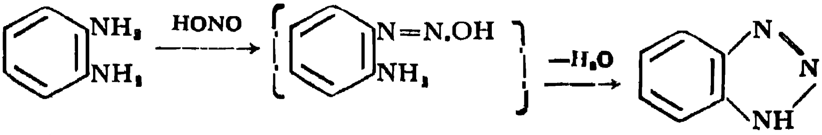
It is a white crystalline solid (m.p. 375K) which readily turns brown in air due to oxidation. It gives the usual reactions of $-NH_2$ group attached to the nucleus in duplicate. Its most characteristic property is the ease with which it gives heterocyclic compounds. For example,

(*i*) *When heated with organic acids.*



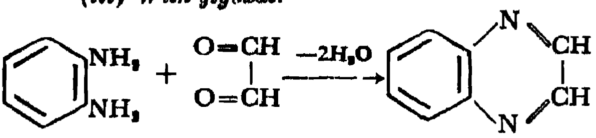
(*Intermediate compound.*) Benziminozole

(*ii*) *With nitrous acid* ($NaNO_2+CH_3COOH$).



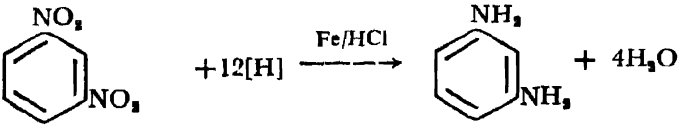
Benztriazole

(*iii*) ***With glyoxal.***

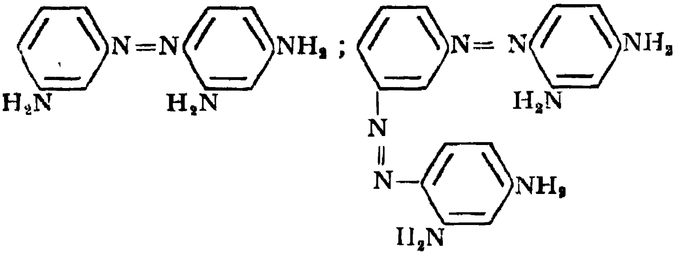


Quinoxaline

***m*-Phenylenediamine** (*1, 3-Benzenediamine*). It is best prepared by the reduction of *m*-dinitrobenzene with iron and hydrochloric acid.



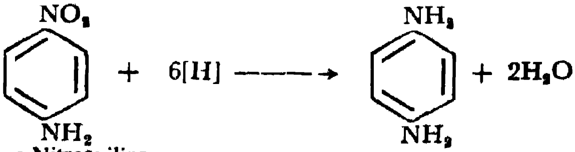
It is a white crystalline solid (m.p. 336K) which turns brown on standing in air. It gives the usual reactions of a diacid base. Its most characteristic property is formation of *Bismark Brown* (a brown dye) when treated with nitrous acid — a monoazo- and a bisazo compound are both formed.



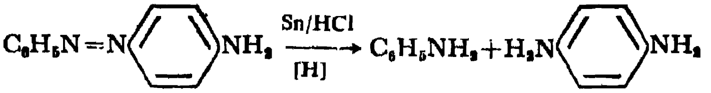
The reaction is used as a sensitive test for detection of traces of nitrites in water or in the qualitative analysis.

m-Phenylenediamine is used in the preparation of dyes.

***p*-Phenylenediamine** (*1, 4-Benzenediamine*). It may be prepared by the reduction of *p*-nitroaniline or *p*-aminoazobenzene.

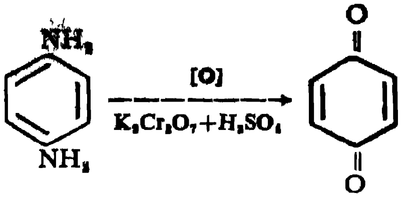


p-Nitroaniline



p-Aminoazobenzene Aniline *p*-Phenylenediamine

It is a white crystalline solid (m.p. 420K) and gives *p*-benzoquinone on vigorous oxidation with potassium dichromate and lphuric acid.



It can be diazotised and thus used in the manufacture of dyes. It is also an excellent photographic developer.

SECONDARY AMINO-COMPOUNDS

12. Diphenylamine, $(C_6H_5)_2NH$.

Preparation. Diphenylamine is prepared—

(1) *By heating phenol with aniline in the presence of zinc chloride at 530K.*

$$\underset{\text{Phenol}}{C_6H_5OH} + \underset{\text{Aniline}}{C_6H_5NH_2} \xrightarrow[530K]{ZnCl_2} \underset{\text{Diphenylamine}}{(C_6H_5)_2NH} + H_2O$$

(2) *By refluxing acetanilide with bromobenzene, potassium carbonate and a little copper powder (catalyst) in nitrobenzene solution* (**Ullmann reaction**).

$$C_6H_5NH.COCH_3 + C_6H_5Br + K_2CO_3 \xrightarrow{Cu} \underset{\text{Diphenylamine}}{(C_6H_5)_2NH} + CO_2 + CH_3COOK + KBr$$

(3) **Manufacture.** *By heating aniline with aniline hydrochloride at 410K under pressure.*

$$C_6H_5NH_2 + C_6H_5NH_2.HCl \longrightarrow (C_6H_5)_2NH + NH_4Cl \ (g.)$$

Properties. It is a colourless, pleasant-smelling crystalline solid (m.p. 327K) practically insoluble in water but readily soluble in alcohol and ether. It resembles aliphatic secondary amines in a number of respects. Some of its characteristic reactions are :

(*i*) *Basic nature.* It is a weaker base than aniline (*cf.* dimethylamine which is a stronger base than methylamine) and forms salts which are completely hydrolysed in solution. This shows that the basic nature decreases with the introduction of phenyl groups in the molecule.

(*ii*) *With sodium.* On heating with metallic sodium or sodamide, diphenylamine forms a sodio derivative more readily than aniline.

$$2(C_6H_5)_2NH + 2Na \longrightarrow 2(C_6H_5)_2N.Na + H_2$$

(*iii*) *With nitrous acid.* It forms *N*-nitrosodiphenylamine with nitrous acid.

$$(C_6H_5)_2N|\overline{\underline{H \ + \ HO}}NO \longrightarrow \underset{\substack{N\text{-nitroso-}\\ \text{diphenylamine}}}{(C_6H_5)_2N.NO} + H_2O$$

(*iv*) *With conc. H_2SO_4 and nitrates.* Its solution in conc. H_2SO_4 gives an intense blue colour with nitrates. This forms a sensitive test for nitrates.

Uses. Diphenylamine is used :

(*i*) *In making certain dyes.*

(*ii*) As a reagent in the detection of nitrates.

(*iii*) As an indicator in oxidation titrations.

(*iv*) As a stabilizer for explosives.

13. *N*-Methylaniline, *N*-Methylphenylamine or *N*-methylbenzenamine, $C_6H_5.NHCH_3$.

Preparation. (*i*) *By heating aniline with methyl iodide calculated quantity*)

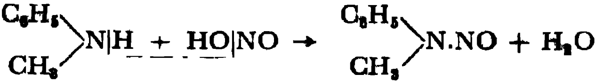
$$C_6H_5NH_2 + CH_3I \longrightarrow \underset{N\text{-Methylaniline}}{C_6H_5NH.CH_3} + HI$$

(*ii*) **Manufacture.** By heating aniline with methanol (1·2 moles) and sulphuric acid at 500K under pressure.

$$C_6H_5NH_2 + \underset{\text{Methanol}}{CH_3OH} \xrightarrow[500K]{H_2SO_4} \underset{N\text{-Methylaniline}}{C_6H_5NH.CH_3} + H_2O$$

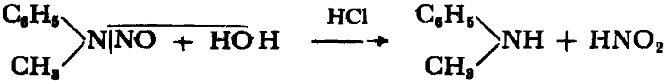
Properties. It is a colourless liquid (b.p. 467K). *N*-Methylaniline is a stronger base than aniline as explained on page *2·556*. It resembles aliphatic secondary amines in many ways but differs from them in substitution reactions of the benzene nucleus (it is substituted in the *o*- and *p*- positions). Some of its important reactions are :

(*i*) With nitrous acid it forms pale-yellow *N*-nitrosoamine which gives Liebermann's nitroso-reaction



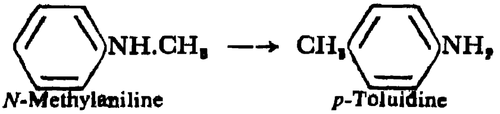
$$\begin{matrix}C_6H_5\\CH_3\end{matrix}\!\!>\!N|\underline{H + HO}|NO \rightarrow \begin{matrix}C_6H_5\\CH_3\end{matrix}\!\!>\!N.NO + H_2O$$

The nitrosoamine gives back *N*-methylaniline on heating with hydrochloric acid



$$\begin{matrix}C_6H_5\\CH_3\end{matrix}\!\!>\!N|\overline{NO + HO}\,H \xrightarrow{HCl} \begin{matrix}C_6H_5\\CH_3\end{matrix}\!\!>\!NH + HNO_2$$

(*ii*) On heating *N*-methylaniline hydrochloride, the $—CH_3$ group migrates to the *p*-position to give toluidine.



TERTIARY AMINO-COMPOUNDS

14. Triphenylamine, $(C_6H_5)_3N$.—It may be prepared—

(*i*) *By heating sodio-diphenylamine with bromobenzene.*

$$(C_6H_5)_2N|\overline{\underline{Na + Br}}|C_6H_5 \longrightarrow (C_6H_5)_3N + NaBr$$

(*ii*) *By heating diphenylamine with iodobenzene, potassium carbonate and a little copper powder (catalyst) in nitrobenzene solution* **(Ullmann reaction).**

$$2(C_6H_5)_2NH + 2C_6H_5I + K_2CO_3 \xrightarrow{Cu} \underset{\text{Triphenylamine}}{2(C_6H_5)_3N} + CO_2 + 2KI + H_2O \quad (v.g.)$$

Properties. It is a colourless, crystalline solid (m.p. 400K) and is too weak a base to form salts with acid. It gives a blue solution when dissolved in concentrated sulphuric acid.

15. *N*,*N*-**Dimethylaniline, $C_6H_5N(CH_3)_2$.**—It may be prepared—

(*i*) *By heating aniline with excess of methyl iodide.*

$$\underset{\text{Aniline}}{C_6H_5NH_2} \xrightarrow[-HI]{CH_3I} \underset{N\text{-Methylaniline}}{C_6H_5NHCH_3} \xrightarrow[-HI]{CH_3I} \underset{N,N\text{-Dimethylaniline}}{C_6H_5N(CH_3)_2}$$

(*ii*) *By heating aniline with methanol (in excess) and sulphuric acid at 500K under pressure.*

$$C_6H_5NH_2 + 2CH_3OH \xrightarrow{H_2SO_4,\ 500K} C_6H_5N(CH_3)_2 + 2H_2O$$

N,*N*-Dimethylaniline is the main product (95%) in the mixture obtained in which *N*-methylaniline and aniline are also present. It is separated by acetylating the mixture and distilling off *N*,*N*-dimethylaniline.

(*iii*) *By hydrogenation of aniline and formaldehyde mixture in aqueous alcoholic sulphuric acid in the presence of platinum catalyst.*

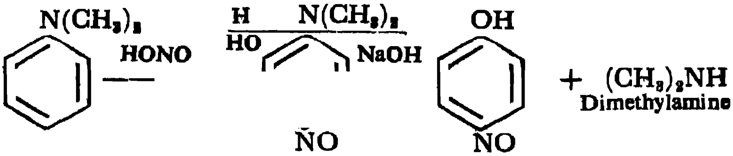
$$C_6H_5NH_2 + 2HCHO + 2H_2 \xrightarrow{Pt} C_6H_5N(CH_3)_2 + 2H_2O \quad (g.)$$

This is an interesting example of *reductive methylation.*

Properties. It is an oily liquid (b.p. 466K). Like *N*-methylaniline, it is a stronger base than aniline as explained on page *2·556*.

It resembles aliphatic tertiary amines, *e.g.*, it gives quaternary compounds with alkyl halides but differs from them in that they can undergo substitution reactions (in the *o*- and *p*- positions) due to the presence of benzene nucleus. Some of its characteristic reactions are :

(*i*) *With nitrous acid.* It reacts with nitrous acid to give *p*-nitroso-dimethylaniline which on boiling with alkali produces *p*-nitrosophenol and dimethylamine.

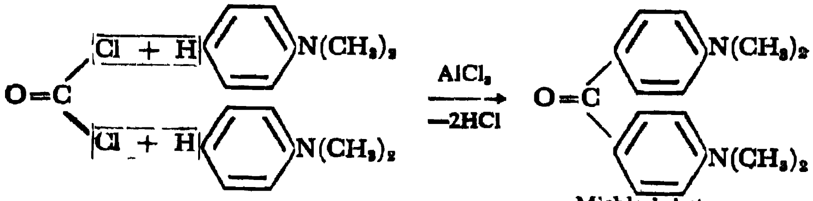


N,*N*-Dimethyl-aniline

p-nitroso-*N*,*N*-dimethylaniline

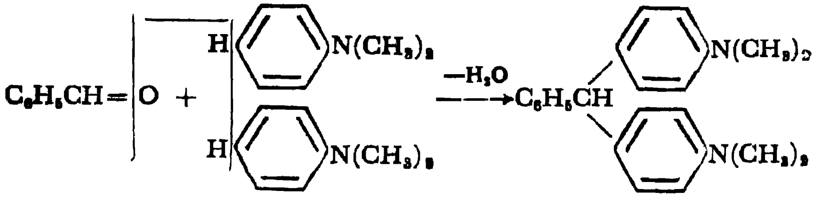
p-nitroso-phenol

(*ii*) *With HCHO or $COCl_2$.* The —$N(CH_3)_2$ group activates the p-hydrogen atom so much that *N*,*N*-dimethylaniline condenses with formaldehyde and carbonyl chloride to form diphenylmethane and benzophenone derivatives respectively.

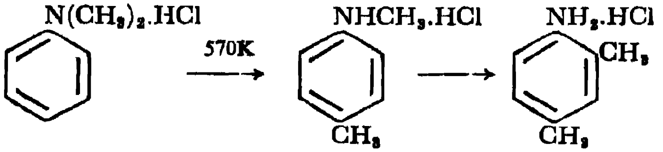


Michler's ketone

Similarly it condenses with aromatic aldehydes to give triphenylmethane derivative.



(*iii*) *Rearrangement.* *N*,*N*-Dimethylaniline hydrchloride undergoes rearrangement on strong heating under pressure. One methyl group migrates to the *p*-position and the second to the *o*-position.



This reaction is known as **Hofmann-Martius rearrangement** and is employed to prepare homologues of aniline.

Uses. It is used as a dye intermediate and for preparing dimethylamine.

ARALIPHATIC AMINES

16. Benzylamine, $C_6H_5CH_2NH_2$.—It is a typical primary aromatic amine and is best regarded as phenyl-substituted methylamine.

Preparation. Benzylamine may be prepared :

(*i*) *By the reduction of phenyl cyanide or benzaldoxime.*

$$\underset{\text{Phenyl cyanide}}{C_6H_5.CN} \xrightarrow{Na/C_2H_5OH} \underset{\text{Benzylamine}}{C_6H_5.CH_2NH_2} \xleftarrow{Na/C_2H_5OH} \underset{\text{Benzaldoxime}}{C_6H_5CH{=}NOH}$$

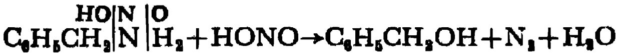
(*ii*) *By heating benzyl chloride with ammonia under pressure.*

$$\underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} + NH_3 \longrightarrow \underset{\text{Benzylamine}}{C_6H_5.CH_2NH_2} + HCl$$

(*iii*) *By the action of bromine and caustic potash on phenylacetamide* (**Hofmann degradation**).

$$\underset{\text{Phenylacetamide}}{C_6H_5CH_2CONH_2} \xrightarrow{Br_2/KOH} \underset{\text{Benzylamine}}{C_6H_5CH_2NH_2}$$

Properties. Benzylamine is a colourless liquid (b.p. 458K) having a characteristic ammoniacal odour resembling aliphatic amines. It differs from aniline in being soluble in water and in being more basic. With nitrous acid it gives benzyl alcohol and no diazonium salt.



$$C_6H_5CH_2NH_2+HONO \rightarrow C_6H_5CH_2OH+N_2+H_2O$$

On the other hand, it closely resembles aliphatic amines in chemical behaviour. When oxidised with potassium permanganate it gives benzoic acid.

$$\underset{\text{Benzylamine}}{C_6H_5CH_2NH_2} \xrightarrow{[O]} \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

17. Distinguishing tests for Different Amines. *See* page 2·572.

QUESTIONS

Essay Type :

1. How is aniline prepared in a state of purity in the laboratory ? Why is aniline less basic than methylamine ? How will you prepare the following from aniline :

(*i*) Iodobenzene ; (*ii*) Sulphanilic acid ;
(*iii*) Phenol ? (*Ravi Shankar B.Sc. 1972*)

2. With the help of a neat diagram describe a method for the preparation of aniline. How is aniline purified ? How does it react with :

(*i*) CH_3I, (*ii*) HNO_2, (*iii*) $CHCl_3$ and KOH, (*iv*) fuming H_2SO_4 ? (*Nagpur B.Sc. 1973*)

3. How is pure aniline manufactured ? How will you convert aniline into acetanilide, sulphanilic acid, phenylhydrazine, diphenylamine, dimethylaniline, thiocarbanilide, *o*-toluidine, diphenylthiourea, benzenediazonium chloride. (*Delhi B.Sc., 1981*)

4. Describe the preparation of Phenylhydrazine. How can you convert it into (*i*) Aniline, and (*ii*) Antipyrene ? (*Rajasthan B.Sc. 1970*)

5. How is Aniline prepared ? Discuss the various methods for distinguishing between Aniline, *N*-Methylaniline and *N*,*N*-Dimethylaniline.

6. (*a*) Draw structures and give names of isomeric aromatic amines of the formula C_7H_9N. How will you distinguish them from one another ? (*Rajasthan B.Sc. 1971*)

(*b*) What happens when—

(*i*) Aniline and Methyl alcohol vapours are passed over activated alumina at 520K.

(*ii*) HNO_2 reacts with *N*, *N*-dimethylaniline ?

Short Answer Type :

1. What happens when aniline is
   (*a*) warmed with $CHCl_3$ and KOH,
   (*b*) treated with cold $NaNO_2$ solution and HCl
   (*c*) acetylated ? (*Delhi B.Sc. Hons. Sub. 1976 Supp.*)
2. Explain why aniline is less basic than ammonia. (*Delhi B.Sc. 1978, 1976 Supp.*)
3. Why is aniline less basic than *N*-methylaniline ? (*Nagpur B.Sc. 1973*)
4. Give a brief account of the chemistry of *N*-methylaniline. (*Sri Venkateshwara B.Sc. 1972*)

Distinguishing Tests for Different Amines

Treat with	PRIMARY			SECONDARY		TERTIARY	
	Aromatic amines $ArNH_2$	Araliphatic amines $ArCH_2NH_2$	Aliphatic amines RNH_2	Aromatic $ArNHAr$	Aliphatic $RNHR$	Aromatic Ar_3N	Aliphatic R_3N
(*i*) Chloroform +alcoholic potash—warm	Carbylamine produced	Carbylamine produced	Carbylamine produced	No action	No action	No action	No action
(*ii*) Nitrous acid ($NaNO_2$+HCl)	Form diazo-compounds in cold and phenols in hot.	Form aromatic alcohols and N_2	Form alcohols and N_2	Give nitroso-amines (*yellow*)	Give nitroso-amines (*yellow*)	Give green nitroso-compounds	Give nitroso-amine and alcohol on warming.
(*iii*) Alkyl halides (*Heat under pressure*) (*Alkylation*)	React with three molecules	React with three molecules	React with three molecules	React with two molecules	React with two molecules	Combine with one molecule under ordinary pressure	Combine with one molecule under ordinary pressure.
(*iv*) Hinsberg's reagent ($C_6H_5SO_2Cl$)	The product is soluble in NaOH	The product is soluble in NaOH	The product is soluble in NaOH	The product is insoluble in NaOH ; soluble in ether	The product is insoluble in NaOH ; soluble in ether	No action	No action.
(*v*) Conc. H_2SO_4 ; conc. HNO_3 ; or Cl_2	Easily sulphonated, nitrated and chlorinated.		No action.	Reactions are possible.	No action	Reactions are possible	No action.

5. Give one method of preparation of each of the following :

(a) Acetanilide, (b) *N*-Methylaniline. (*Kerala B.Sc. 1973*)

6. What are the products obtained when :

(*i*) Acetanilide is treated with bromine ;

(*ii*) *N*-Methylaniline is acted upon by nitrous acid ? (***Kerala B.Sc. 1973***)

7. Write mechanism for the ammonolysis of halogeno-compounds with liquid ammonia giving necessary conditions.

8. Write canonical forms of the resonance hybrid of aniline. Does anilinium ion show resonance ?

9. What happens when the following are strongly heated ?

(*i*) Methylaniline hydrochloride,

(*ii*) Dimethylaniline hydrochloride.

10. What do you understand from :

(*i*) Hofmann degradation ;

(*ii*) Hofmann-Martius rearrangement ?

11. Write equations for these reactions, between :

(1) (*a*) Nitrobenzene or Nitrosobenzene+tin+hydrochloric acid or iron +hydrochloric acid. (*b*) Chlorobenzene+ammonia+cuprous oxide.

(2) Aniline+(*i*) H_2SO_4 ; (*ii*) CH_3COCl ; (*iii*) benzoyl chloride ; (*iv*) methyl iodide ; (*v*) chloroform+alcoholic potash ; (*vi*) $NaNO_2$+HCl (ice-cold and hot) ; (*vii*) Grignard reagent ; (*viii*) $COCl_2$; (*ix*) CS_2.

(3) Aniline+(*i*) benzaldehyde ; (*ii*) hypochlorous acid ; (*iii*) acidified potassium permanganate ; (*iv*) sodium ; (*v*) benzenediazonium chloride ; (*vi*) bromine ; (*vii*) fuming sulphuric acid.

(4) Sulphanilic acid+(*i*) HNO_3 ; (*ii*) Br_2.

12. What happens when the following react ? Give equations.

(1) Acetanilide+(*i*) chlorosulphonic acid followed by reaction with NH_3 and hydrolysis ; (*ii*) HNO_3 followed by hydrolysis ; (*iii*) $C_6H_5Br+K_2CO_3+Cu$ powder.

(2) (*a*) Methylaniline+(*i*) HNO_2 ; (*ii*) Heating. (*b*) Aniline+HCHO+H_2.

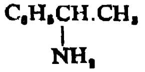
(3) (*a*) Dimethylaniline+(*i*) HNO_2 ; (*ii*) HCHO or $COCl_2$; (*iii*) C_6H_5CHO ; (*iv*) Heating. (*b*) Reduction of (*i*) phenyl cyanide ; (*ii*) benzaldoxime.

(4) Benzylamine+(*i*) nitrous acid ; (*ii*) acetyl chloride ; (*iii*) chloroform +alcoholic potash ; (*iv*) potassium permanganate.

13. Diphenylamine, $(C_6H_5)_2NH$ ($K_b=6\times10^{-14}$) is a far weaker base than aniline ($K_b=3{\cdot}8\times10^{-10}$). How do you explain the difference on the basis of their resonance structures ?

14. *p*-Toluidine and *p*-anisidine (*p*-$CH_3O-C_6H_4-NH_2$) are stronger bases than aniline whereas *p*-chloroaniline and *p*-nitroaniline are weaker bases. Explain, why.

15. How will you prepare the following amines through reductive amination.

(*a*)  $C_6H_5\underset{\displaystyle NH_2}{\underset{|}{CH}}.CH_3$ (*b*) $C_6H_5CH_2NH_2$.

16. Reductive amination of a ketone is a better method for preparation of amines of the type $\begin{matrix}R\\R'\end{matrix}\!\!>\!CHNH_2$ than ammonolysis of alkyl halides. Explain why.

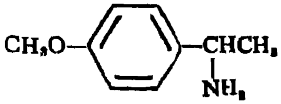
17. How will you bring about the following transformation making use of reduction of an amide or nitrile ?

Benzoic acid→*N*-ethylbenzylamine.

18. **How will you carry out the following transformations :**

(*i*) Methoxybenzene→*p*-methoxyaniline

(*ii*) Methoxybenzene →



(*iii*) Toluene→Benzyl-trimethylammonium chloride, $C_6H_5CH_2N^+(CH_3)_3\ Cl^-$

(*iv*) *p*-nitrotoluene→*p*-nitroaniline.

19. Para nitrosation of *N,N*-dimethylaniline $C_6H_5N(CH_3)_2$ is an example of *C*-nitrosation believed to be a nucleophilic substitution reaction in which NO^+ ion is the nucleophile.

(*a*) Explain how NO^+ ions are formed in an aqueous solution of $NaNO_2$ and HCl.

(*b*) Write the steps involved to explain the mechanism of the above *C*-nitrosation.

20. Tertiary aromatic amines and phenols undergo *C*-nitrosation reaction whereas most of the other aromatic compounds do not. Assign reasons for this difference in behaviour.

21. How will you prepare benzylamine from each of the following compounds ?

(*a*) Benzyl bromide	(*b*) Benzamide
(*c*) Benzaldehyde	(*d*) Benzonitrile
(*e*) Phenylacetamide	(*f*) Phenylnitromethane.

22. Give structures for products of each of the following reactions.

(*a*) Aniline + propanoyl chloride→

(*b*) *m*-Dinitrobenzene$+H_2S \xrightarrow[C_2H_5OH]{NH_3}$

(*c*) *p*-Toluidine + Br_2 (*excess*) $\xrightarrow{H_2O}$

HINTS

15 (*a*) $C_6H_5COCH_3+NH_3\xrightarrow{H_2,Ni}$

(*b*) $C_6H_5CHO+NH_3\xrightarrow{H_2,\ Ni}$

16. Treatment of secondary alkyl halide with ammonia is always accompanied by some elimination in addition to substitution.

17 $C_6H_5COOH\longrightarrow C_6H_5COCl\xrightarrow{C_2H_5NH_2}C_6H_5\ CONHC_2H_5\xrightarrow{H_2,\ Ni}C_6H_5CH_2NHC_2H_5$

18. (*i*) Methoxybenzene$\xrightarrow{HNO_3/H_2SO_4}\quad\xrightarrow{Fe+HCl}$

(*ii*) Methoxybenzene$\xrightarrow{CH_3COCl,\ AlCl_3}\quad\xrightarrow{NH_3+H_2+Ni}$

(*iii*) Toluene $\xrightarrow{Cl_2,\ light}\quad\xrightarrow{(CH_3)_3N}$
]

(*iv*) p-nitrotoluene $\xrightarrow[(ii)\ H_3O^+]{(i)\ KMnO_4,\ OH^-}$ p-nitrobenzoic acid

$\longrightarrow$ SO_2Cl_2 followed by NH_3 $\longrightarrow$ Br_2+KOH

Problems :

1. An aromatic compound C_6H_7N (A) on heating with a calculated quantity of CH_3I gives C_7H_9N (B) which reacts with nitrous acid to form $C_7H_8N_2O$ (C). Hydrochloride of (B) on heating isomerises to another compound D. Compound C on heating with hydrochloric acid regenerates B. Identify the various compounds A to D and write chemical equations for the various reactions involved.

2. An organic compound C_6H_7N (A) forms salts with acids. On heating A with excess methanol and sulphuric acid at 500K under pressure another compound $C_8H_{11}N$ (B) was obtained. B reacts with nitrous acid to give $C_8H_{10}N_2O$ (C) which on boiling with NaOH gives $C_6H_5O_2N$ (D). Hydrochloride of B on heating to 570K gives an isomeric compound E. Identify the various compounds A to E and write chemical equations for the various reactions involved.

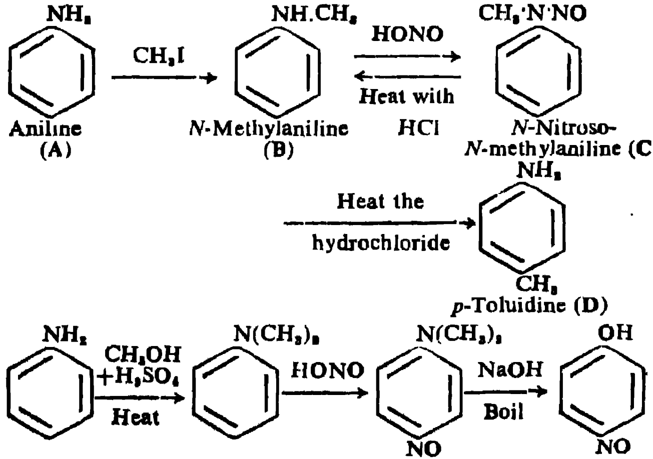
3. An aromatic compound contains C=79·34 per cent ; H=9·09 per cent and N=11·57 per cent. Its vapour density is 60·5.

Write the structural formulae of the various isomers of this compound. Describe the reactions of nitrous acid on them.

4. C_7H_9N (A) is an amine which reacts with Hinsberg's reagent and the product dissolves in NaOH to give a clear solution. This on acidification gives a precipitate. A on treatment with an ice-cold solution of $NaNO_2$ and HCl followed by treatment with β-naphthol gives an intensely coloured compound. A gives a single strong absorption peak in the region 680-810 cm⁻¹ at 815 cm⁻¹. Identify the amine A.

ANSWERS

1.



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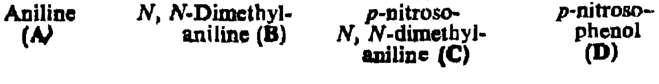
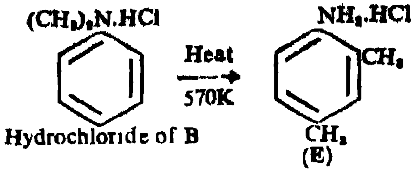


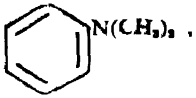


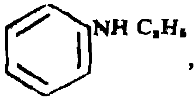
Hydrochloride of B

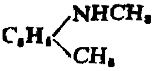
(E)

3 Molecular formula $= C_8H_{11}N$.

Structural formulae of various isomers

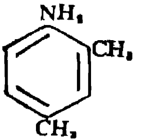




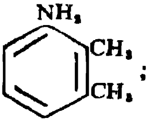


$C_6H_4\begin{cases}NHCH_3\\CH_3\end{cases}$

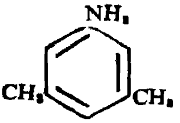
o-, m-, and p-



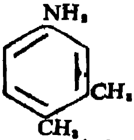
2, 4-Dimethyl-aniline



2, 3-Dimethyl-aniline



3, 5-Dimethyl-aniline



3, 4-Dimethyl-aniline

4 (*i*) Hinsberg's reaction suggests it is a primary amine.

(*ii*) Coupling with β-naphthol suggests that it is an aromatic amine (not araliphatic)

(*iii*) It must be $CH_3-C_6H_4-NH_2$ (Toluidine)

(*iv*) Absorption spectra suggests that it is *p*-Toluidine.

41

Diazonium Salts

1. Diazotisation.—Peter Griess, a German chemist, in 1858 observed that when a primary aromatic amino-compound such as aniline or toluidine was treated with an ice-cold solution of nitrous acid, the product was an unstable compound known as an *arene diazonium salt* or a *diazo-compound.* It was so called, for it contains the di-azo group, —N_2—(*Di*=two ; *azo* from French *azote*=nitrogen).

$$\underset{\text{Primary aromatic amine}}{Ar.NH_2} + HNO_2 + HCl \longrightarrow \underset{\text{Arenediazonium chloride}}{Ar.N_2Cl} + H_2O$$

These are the salts of the strong base *arenediazonium hydroxide*, $Ar.N_2.OH$, which is known only in aqueous solution and has not yet been isolated. *The formation of a diazonium salt by the interaction of primary aromatic amine, sodium nitrite solution and an inorganic acid in ice-cold solution is known as* **diazotisation**.

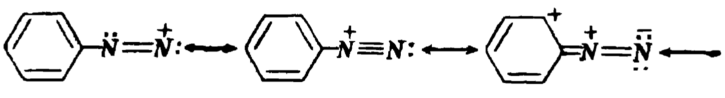
When primary aliphatic amine is treated with nitrous acid, the amino-group is replaced by an —OH group, and nitrogen evolved.

$$RNH_2 + HNO_2 \longrightarrow ROH + N_2 + H_2O$$

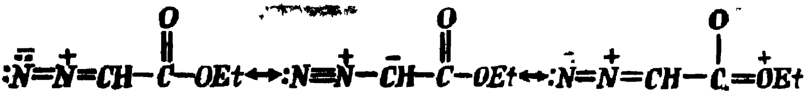
Diazo-compounds may be obtained from aliphatic compounds containing primary amino-group ($-NH_2$) provided the amino-group is attached to a carbon atom which is adjacent to an electron-withdrawing group like —CN (cyano), —COR (acyl) or —COOR (carboalkoxy). For example, aminoacetic ester forms diazoacetic ester.

$$\underset{\text{Ethylglycine}}{CH_2(NH_2)COOC_2H_5} \xrightarrow{\text{HONO}} \underset{\text{Ethyl diazoacetate}}{N_2CH\,COOC_2H_5}$$

Greater stability of the arenediazonium salts (ArN_2^+) as compared to aliphatic analogues (RN_2^+) may be explained in terms of resonance which involves the benzene ring too.



The fact that aliphatic diazo-compounds are stabilised by the presence of a group like —CN, —COR or —COOR is also attributed to resonance. For example, diazoacetic ester is more stable than diazomethane due to extended resonance in the former.



$$:\overset{-}{N}=\overset{+}{N}=CH-\overset{\overset{O}{\|}}{C}-OEt \longleftrightarrow :N\equiv\overset{+}{N}-\overset{-}{C}H-\overset{\overset{O}{\|}}{C}-OEt \longleftrightarrow :\overset{-}{N}=\overset{+}{N}=CH-\overset{\overset{O^-}{|}}{C}=\overset{+}{O}Et$$

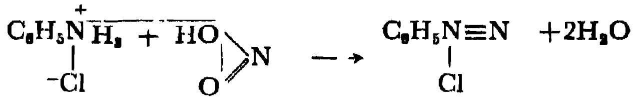
2. Nomenclature.—The diazonium salts are named by adding 'diazonium chloride', 'diazonium sulphate', etc., to the name of the parent hydrocarbon. For example, $C_6H_5N_2Cl$ is benzenediazonium chloride, $C_6H_5N_2.HSO_4$ is benzenediazonium sulphate while $p\text{-}CH_3.C_6H_4N_2HSO_4$ is *p*-toluenediazonium sulphate.

3. Benzenediazonium chloride, $C_6H_5N_2Cl$.

Preparation. Benzenediazonium chloride is prepared by treating an ice-cold solution of aniline in hydrochloric acid with an ice-cold solution of sodium nitrite with constant stirring. Presence of some free nitrous acid (turns starch iodide paper blue) indicates that the reaction is complete.

$$NaNO_2 + HCl \longrightarrow NaCl + HNO_2$$

$$C_6H_5NH_2 + HCl \longrightarrow \underset{\text{Phenylammonium chloride}}{[C_6H_5NH_3]^+Cl^-}$$



$$C_6H_5\overset{+}{N}H_2\text{–}Cl + HO\text{–}N{=}O \longrightarrow C_6H_5N{\equiv}N\text{–}Cl + 2H_2O$$

Benzenediazonium chloride
(*Blomstrand formula*)

It is unstable and is, therefore, seldom isolated in dry state. Its ice-cold solution obtained above is used as such wherever needed. If, however, crystals of benzenediazonium chloride are needed, these are prepared by treating an ice-cold solution of aniline in absolute alcohol with concentrated hydrochloric acid and then adding amyl nitrite drop by drop. On standing and cooling crystals of benzenediazonium choride separate.

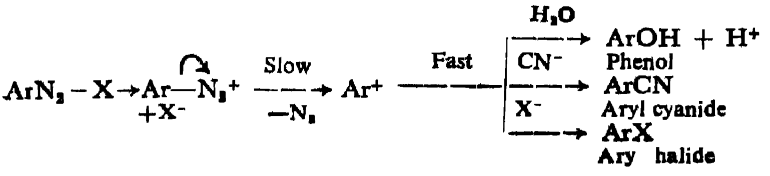
Diazotisation on a commercial scale is done similarly in the manufacture of dyes.

The acid used is taken in excess to keep the mixture strongly acidic which is necessary to prevent coupling of benzenediazonium chloride with excess of aniline (see page *2 582*). Since excess of nitrous acid present in benzenediazonium chloride solution interferes with its subsequent reactions, it is destroyed by addition of small quantity of urea.

Properties : Physical. Benzenediazonium chloride is a colourless, crystalline solid, readily soluble in water but it is less soluble in alcohol. It turns brown on exposure to air. While quite harmless in aqueous solution it is dangerously explosive in the dry state.

Chemical. Reactions of benzenediazonium chloride are the general reactions of diazonium salts and may be divided into two groups : (*i*) Those involving displacement of the diazo-group by another univalent group with the liberation of nitrogen gas, and (*ii*) those in which the two nitrogen atoms are retained.

(*a*) **Replacement Reactions.** The replacement reactions are examples of unimolecular nucleophilic substitution (S_N1).



(1) *Replacement by Hydroxyl Group.* **Benzenediazonium chloride solution on boiling or when steam distilled gives Phenol** (the diazo-group is replaced by hydroxyl group.)

$$C_6H_5\underline{N_2Cl + H}OH \longrightarrow \underset{\text{Phenol}}{C_6H_5OH} + N_2 + HCl$$

(2) *Replacement of Hydrogen.* On reduction with sodium stannite (alkaline stannous chloride), or hypophosphorous acid (most useful) benzenediazonium chloride gives **benzene** (diazo-group replaced by hydrogen atom).

$$C_6H_5N_2^+Cl^- + H_3PO_2 + H_2O \longrightarrow C_6H_6 + N_2 + H_3PO_3 + HCl$$

An especially elegant way of carrying this replacement is to use hypophosphorous acid as diazotising agent, the diazonium salt is reduced as fast as it is formed.

This reaction provides a method of removing an $—NH_2$ or $—NO_2$ group from an aromatic ring.

(3) *Replacement by Halogens.*

(*a*) **Sandmeyer Reaction** (1884). When benzenediazonium chloride solution is added to a solution of cuprous halide dissolved in corresponding halogen acid, a phenyl halide is obtained (diazo-group is replaced by a halogen atom).

$$C_6H_5N_2Cl \xrightarrow{\text{CuCl/HCl}} \underset{\text{Chlorobenzene}}{C_6H_5Cl} + N_2 \quad (g.)$$

$$C_6H_5N_2Cl \xrightarrow{\text{CuBr HBr}} \underset{\text{Bromobenzene}}{C_6H_5Br} + N_2 \quad (g.)$$

The mechanism of the reaction is uncertain but possibly the reaction proceeds through free radical mechanism as given below :

(*i*) Cuprous chloride or bromide gives a complex ion, *e.g.*, $CuCl_2^-$.

$$CuCl + Cl^- \longrightarrow CuCl_2^-$$

(*ii*) The diazonium salt reacts with the complex ion when aryl radical it believed to be generated by an electron transfer, coupled with loss of nitrogen.

$$ArN_2^+ + Cu—Cl_2 \xrightarrow{\text{Slow}} N_2 + Ar^{\cdot} + Cu—Cl_2$$

(*iii*) Finally the free radical abstracts a chlorine atom from cupric chloride.

$$Ar^{\cdot} + Cl—Cu—Cl \xrightarrow{\text{Fast}} ArCl + CuCl$$

(*b*) **Gattermann Reaction** (1890). Cuprous salts used as catalyst in the Sandmeyer reaction are replaced by finely divided copper in this reaction. The rest of the process is similar to the Sandmeyer reaction.

$$C_6H_5N_2Cl \xrightarrow{\text{Cu}} C_6H_5Cl + N_2$$

$$C_6H_5N_2Br \xrightarrow{\text{Cu}} C_6H_5Br + N_2$$

(*c*) **Iodo-compounds.** On boiling benzenediazonium chloride with aqueous potassium iodide solution, the diazo-group is replaced by iodine atom and constitutes the best method for introducing an iodine atom into the benzene ring.

$$C_6H_5|\underline{N_2Cl + K}|I \longrightarrow C_6H_5I + N_2 + KCl \qquad (74\text{-}76\%)$$

(*d*) **Fluoro-compounds.** Replacement of diazonium group by —F is carried out by treating arenediazonium salt solution with fluoboric acid, HBF_4 when arenediazonium fluoborate, $ArN_2^+BF_4^-$ is precipitated. This is termed **Schiemann reaction.** This is filtered, washed, dried and heated when dry diazonium fluoborate decomposes to yield aryl fluoride.

$$ArN_2^+X^- \xrightarrow{HBF_4} \underset{\text{ppt}}{ArN_2^+BF_4^-} \xrightarrow{\text{heat}} ArF + BF_3 + N_2$$

Utility of synthesis of aryl halides from diazonium salts. Diazonium salts are used in the preparation of aryl fluorides and iodides which cannot be prepared by direct halogenation. Aryl chlorides and bromides can be prepared by direct halogenation but it is difficult to isolate the pure compound from the mixture of *o*- and *p*-isomers obtained because of similarity of their boiling points. Diazonium salts obtained from nitro compounds (which are available pure) are used for the preparation of bromides and iodides.

(4) *Replacement by a Cyano-group.* Benzenediazonium chloride solution on treatment with cuprous cyanide dissolved in aqueous potassium cyanide, $K_3Cu(CN)_4$ or with aqueous potassium cyanide in the presence of copper powder, gives benzonitrile. This is a special case of Sandmeyer and Gattermann reactions.

$$C_6H_5|N_2Cl + K|CN \xrightarrow{K_3Cu(CN)_4} \underset{\text{Benzonitrile}}{C_6H_5CN} + N_2 + KCl \quad (65\%)$$

$$C_6H_5|\underline{N_2Cl + K}CN \xrightarrow{Cu} C_6H_5CN + N_2 + KCl \quad (60\%)$$

Benzonitrile obtained above can be used for the synthesis of benzoic acid and benzylamine by hydrolysis and reduction respectively.

$$\underset{\text{Benzylamine}}{C_6H_5CH_2NH_2} \xleftarrow{4H} \underset{\text{Benzonitrile}}{C_6H_5C{\equiv}N} \xrightarrow[-NH_3]{2H_2O} \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

(5) *Replacement by Nitro-group.* This is carried out by carrying on diazotisation with nitrous acid in the presence of cuprous oxide.

$$\overline{C_6H_5|N_2Cl + H}|NO_2 \xrightarrow{Cu_2O} \underset{\text{Nitrobenzene}}{C_6H_5NO_2} + N_2 + HCl$$

(6) *Replacement by an Aryl group.* On treating benzenediazonium chloride with ethanol and copper powder diphenyl is produced.

$$2C_6H_5N_2Cl \xrightarrow[Cu]{C_2H_5OH} C_6H_5.C_6H_5 + 2N_2 + 2HCl$$

Diphenyl is also obtained when benzene is added to an alkaline solution of the diazonium salt.

$$C_6H_5N_2Cl + C_6H_6 \xrightarrow{NaOH} C_6H_5C_6H_5 + N_2 + NaCl + H_2O$$

The reaction is termed **Gomberg Reaction.**

The reaction takes place by a free radical mechanism.

$$C_6H_5N_2^+Cl^- \xrightarrow{-OH^-} C_6H_5-N=N-OH \longrightarrow C_6H_5^{\cdot} + N_2 + {}^{\cdot}OH$$

$$C_6H_5^{\cdot} + C_6H_6 + {}^{\cdot}OH \longrightarrow C_6H_5-C_6H_5 + H_2O$$

Meerwein reaction. Diazonium salts add to compounds containing activated ethylenic bond in acetone solution in presence of cupric salt. For example benzenediazonium chloride adds to acrylonitrile with elimination of nitrogen. The mechanism is uncertain but is generally considered to be homolytic addition occurring at the β-position. It is because free radical obtained from α-addition is less stable than the one formed from β-addition.

$$C_6H_5^{\cdot} + CH_2=CHCN \longrightarrow C_6H_5CH_2-{}^{\cdot}CHCN$$

$$\xrightarrow{Cu^{2+}} Cu^+ + C_6H_5CH_2\overset{+}{C}HCN \xrightarrow{Cl^-} C_6H_5CH_2CHClCN$$

Addition to α, β- unsaturated acid is accompanied by decarboxylation, *e.g.*, benzenediazonium chloride adds to cinnamic acid to give stilbene.

$$\underset{}{C_6H_5N_2^+Cl^-} + \underset{\text{cinnamic acid}}{C_6H_5CH=CHCOOH} \longrightarrow \underset{\text{stilbene}}{C_6H_5CH=CHC_6H_5} + N_2 + CO_2 + HCl$$

(*b*) **Reactions in which the Diazo-group is retained :**

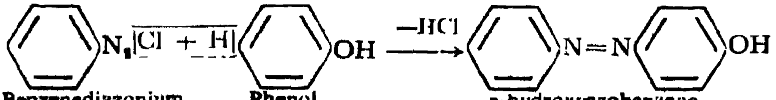
(1) *Reduction.* Benzenediazonium chloride on reduction with stannous chloride and hydrochloric acid or with sodium sulphite gives phenylhydrazine.

$$\underset{\substack{\text{Benzenediazonium}\\\text{chloride}}}{C_6H_5-N=N-Cl} + 4[H] \xrightarrow{SnCl_2/HCl} \underset{\substack{\text{Phenylhydrazine}\\\text{hydrochloride}}}{C_6H_5.NH.NH_2.HCl}$$

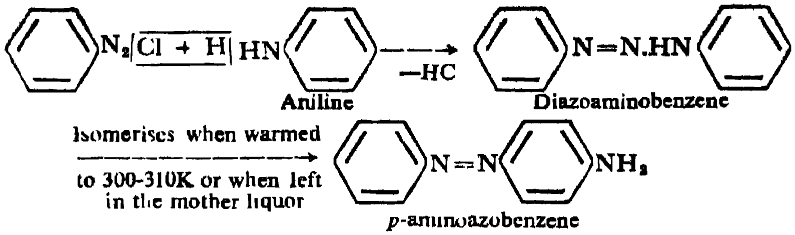
With vigorous reducing agents like Zn + HCl the product is aniline.

$$C_6H_5N_2Cl \xrightarrow{Zn/HCl} [C_6H_5NH.NH_2] \xrightarrow{Zn/HCl} C_6H_5NH_2 + NH_3$$

(2) *Coupling.* It gives azo-dyes by coupling with phenol, aniline or their derivatives.

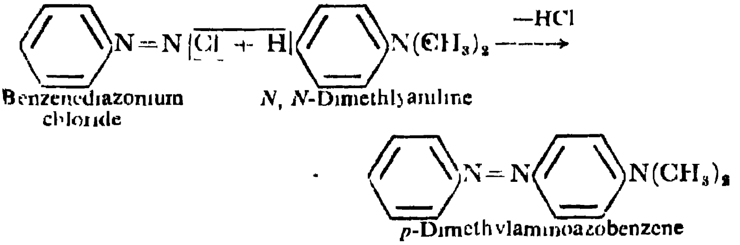


Benzenediazonium chloride **Phenol** *p*-hydroxyazobenzene (*Orange dye*)

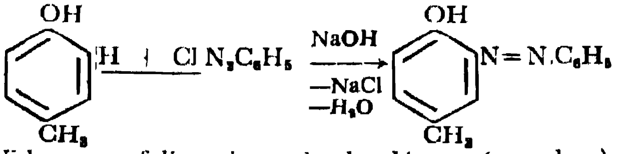


With primary and secondary amines coupling may take place at the nitrogen atom to form diazoamino-compounds (*N*-azo-compounds) or directly with the nucleus to form aminoazo compounds (*C*-azo compounds) depending upon the nature of the amino-compounds and *p*H of the solution.

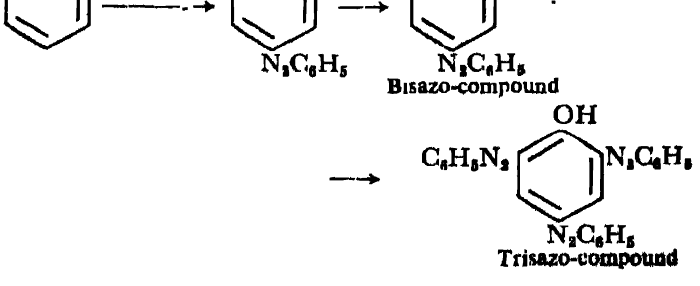
With tertiary amines coupling takes place directly with the nucleus, *e.g.*, *N*,*N*-dimethylaniline.



With phenol coupling is best carried out in faintly alkaline solution and with amines in faintly acid solution. The azo-group enters mainly the *p*-position to the hydroxyl or amino-group but in case this position is not vacant, coupling takes place in the *o*-position but never in the *m*-position. For example, on treating 3-methylphenol with benzenediazonium chloride coupling occurs in the *o*-position.

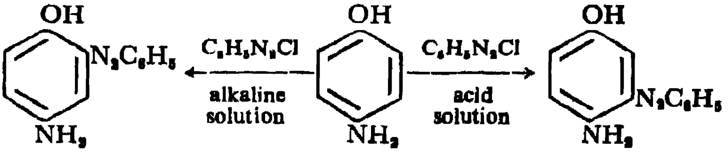


With excess of diazonium salt the *bisazo-* (*o-* and *p-*) and the *trisazo* compound may be produced.

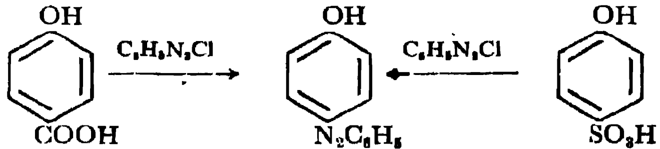


Introduction of second azo-group is facilitated by the presence of an alkyl group in the *p*-position to the hydroxyl group, or by two hydroxyl groups in the *m*-position.

In case a compound contains both —OH and NH_2 groups, the coupling takes place in *o*-position to amino-group in acid solution. In alkaline solution coupling takes place in *o*-position to hydroxyl group.



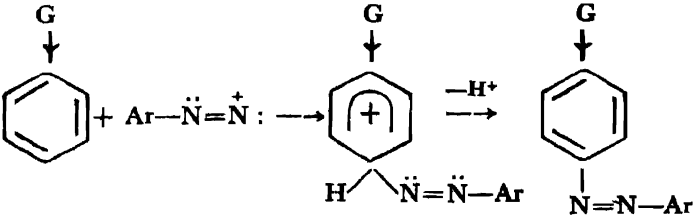
In cases where a —COOH or —SO_3H group is present in *p*-position to —OH, it is replaced by azo-group during coupling.



p-hydroxybenzoic acid *p*-hydroxyazobenzene *p*-hydroxybenzenesulphonic acid

Mechanism of coupling. *Coupling is an electrophilic substitution reaction as the attacking reagent, the arenediazonium ion, ArN_2^+ is an electrophile.* This, being very weakly electrophilic, is capable of attacking only very reactive rings. Coupling is, therefore, activated by electron-releasing groups, generally —OH, —NH_2, —NHR, or NR_2. Arenediazonium ion is a reasonance hybrid of I and II given below :

$$\underset{\text{I}}{\mathrm{Ar{-}\overset{+}{N}{\equiv}N:}} \leftrightarrow \underset{\text{II}}{\mathrm{Ar{-}\overset{..}{N}{=}\overset{+}{N}:}}$$



Since II is the 'reactive' contributing reasonating structure, any factor that increases its contribution will increase the reactivity of the diazonium ion. *Since electron-withdrawing groups would favour (II) and electron-releasing groups would favour (I)*, the diazonium ions with electron-withdrawing groups are more reactive. Thus the *p*-nitrobenzenediazonium cation is 10,000 times as reactive as the *p*-methoxy ion under the same conditions. The 2, 4, 6-trinitrobenzenediazonium cation is so reactive that it couples with mesitylene.

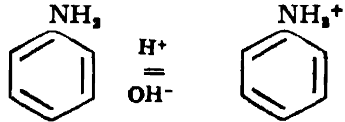
Importance of adjustment of the coupling medium to the right degree of acidity or alkalinity can be explained as follows :

In the presence of OH^- the diazonium ion, ArN_2^+ exists in equilibrium with an unionized compound, $Ar{-}N{=}N{-}OH$ and salts ($Ar{-}N{=}N{-}O^-Na^+$) derived from it, which do not couple.

$$\underset{\text{Couples}}{[Ar{-}N{\equiv}N{:}]^+OH^-} \underset{H^+}{\overset{NaOH}{\rightleftharpoons}} \underset{\text{Does not couple}}{Ar{-}N{=}N{-}OH} \underset{H^+}{\overset{NaOH}{\rightleftharpoons}} \underset{\text{Does not couple}}{Ar{-}N{=}N{-}O^-Na^+}$$

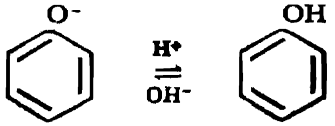
Hence so far as the electrophile is concerned, coupling is favoured by low concentration of OH^-, *i.e.*, by high acidity.

But what is the effect of high acidity on the amine or phenol with which the diazonium salt is reacting ? Acid converts an amine into its ion, which is relatively unreactive due to its positive charge. Hence higher the acidity, lower the rate of coupling.



Couples Does not couple

A phenol is appreciably acidic and in aqueous solution it exists in equilibrium with phenoxide ion.



Couples rapidly Couples slowly

$-O^-$ being more powerfully electron-releasing than $-OH$, the phenoxide ion is more reactive than phenol. The higher the acidity of the medium, the lower the proportion of phenoxide ion and the lower the rate of coupling.

The following conditions under which coupling proceeds most rapidly are the result of a compromise :

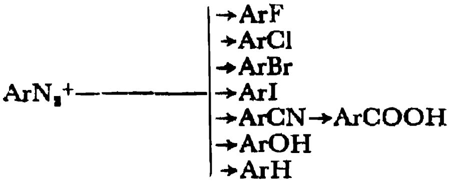
(*i*) The solution must not be so alkaline that the concentration of diazonium ion is too low.

(*ii*) It must not be so acidic that the concentration of free amine or phenoxide ion is too low.

This is why amines couple fastest in mildly acidic solution and phenols couple fastest in mildly alkaline solution.

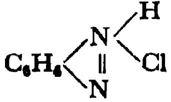
4. Use of Diazonium Salts in Organic Synthesis.—From the properties of benzenediazonium chloride as given earlier we find that diazonium salts are very reactive compounds and give rise to a variety of products, *e.g.*, phenols, hydrocarbons, ethers, halogen derivatives, cyanides, amines, acids, nitro-derivatives, phenylhydrazines and azo-dyes. The amines from which diazonium compounds are prepared are readily obtained from the corresponding nitro compounds, which are prepared by direct nitration. The diazonium salts thus provide a powerful synthetic instrument in the hands of an organic chemist.

$$\mathrm{ArH} \xrightarrow[H_2SO_4]{HNO_3+} \mathrm{ArNO_2} \xrightarrow{H} \mathrm{ArNH_2} \xrightarrow[\substack{+HCl\\273K}]{NaNO_2} \mathrm{ArN_2^+}$$



5. Structure of Benzenediazonium Chloride.

(1) **Griess** (1864) thought that both the nitrogen atoms present in benzenediazonium chloride were attached to the benzene nucleus and assigned the following formula to it.



(2) **Kekule** (1866) believed that only one of the two nitrogen atoms was directly attached to the nucleus as in its various reactions N_2Cl group is replaced by a univalent radical (*e.g.*, OH, Cl, CN, etc.). This view is further confirmed by the fact that tetrabromo-sulphonic acid of aniline yields a diazo-compound in which the four bromine atoms and the sulphonic group are still present. He further suggested the formula

$$C_6H_5{-}N{=}N{-}Cl$$

for benzenediazonium chloride. Kekule's formula is supported by the following reactions of benzenediazonium chloride :

(*i*) Formation of phenylhydrazine by reduction.

(*ii*) Formation of azo-compounds by coupling.

(3) **Blomstrand** (1869) argued that since diazonium salts resemble ammonium salts closely, there must be one pentavalent nitrogen in benzenediazonium chloride as in ammonium chloride.

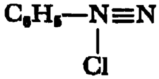
The supposed analogy between diazonium salts and ammonium salts is borne out by the following facts :

(*i*) Both ammonium and diazonium salts form colourless crystals soluble in water.

(*ii*) Salts of both types with strong acids are neutral to litmus while salts with weak acids are alkaline to litmus. For example, chlorides and sulphates are neutral while carbonates and acetates of both types are alkaline to litmus.

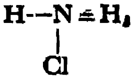
(*iii*) Both the types of salts have practically the same ionization constants.

He suggested the following structural formula for it:



$$C_6H_5—\overset{}{\underset{Cl}{N}}\equiv N$$

Benzenediazonium chloride



$$H—\underset{Cl}{N}\equiv H_3$$

Ammonium chloride

In the modern terminology benzenediazonium chloride is represented by the formula $[C_6H_5—N\equiv N:]^+Cl^-$.

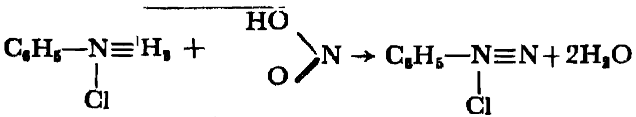
Blomstrand's formula is further supported by the following facts:

(*i*) Electrical conductivity measurements by Goldschmidt (1890) showed that the molecule of diazonium salt dissociates into two ions.

(*ii*) Diazonium compounds are unstable and explosive in the solid state. They differ from azo-compounds which are very stable. The structures of the two must, therefore, be completely different.

(*iii*) From infra-red absorption spectra of diazonium salts, it has been shown in 1955 that there is a triple bond present in diazonium salts.

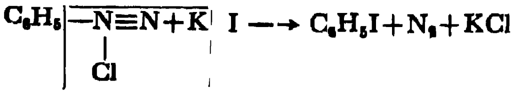
(*iv*) It readily explains the formation of benzenediazonium chloride from aniline which can be diazotised only in the form of its salts.



$$C_6H_5—\underset{Cl}{N}\equiv H_3 + \begin{matrix}HO\\O\end{matrix}\!\!>N \rightarrow C_6H_5—\underset{Cl}{N}\equiv N + 2H_2O$$

Aniline hydrochloride Nitrous acid Benzenediazonium chloride

(*v*) It explains satisfactorily the formation of products obtained by replacement of N_2Cl group by monovalent groups (*e.g.*, Cl, I, CN, etc.) with elimination of nitrogen.



$$C_6H_5—\underset{Cl}{N}\equiv N + KI \longrightarrow C_6H_5I + N_2 + KCl$$

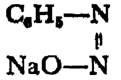
(4) **Von Pechmann** (1892) proposed the nitrosamine structure $C_6H_5NH.NO$ for benzenediazium hydroxide. He explained the two forms of diazoates (diazotates) as structural isomers.

$C_6H_5N=N.OH$ *n*-diazohydroxide → $C_6H_5N=N.ONa$ *n*-diazoate

$C_6H_5NH.NO$ *iso*-diazohydroxide → $C_6H_5.NNa.NO$ *iso*-diazoate

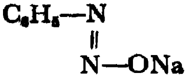
(5) **Hantzsch** (1895) explained the existence of diazoates as geometrical isomers. He adopted the Kekule formula since absence of free rotation about the double bond (—N=N—) can give rise to geometrical isomerism which is not possible with Blomstrand formula.

The two geometrical isomers of diazoates are:



$$\begin{matrix}C_6H_5-N\\ \|\\ NaO-N\end{matrix}$$

Sod. *n*-diazoate
(*syn*-form)



$$\begin{matrix}C_6H_5-N\\ \|\\ N-ONa\end{matrix}$$

Sod. *iso*-diazoate
(*anti*-form)

According to Hantzsch, benzenediazonium chloride has the *Blomstrand formula* $[C_6H_5-N\equiv N]^+Cl^-$ *in acid solution.*

This is the salt of the base benzenediazonium hydroxide $[C_6H_5-N\equiv N]^+OH^-$ which has never been isolated. On making alkaline it gives diazonium hydroxide which rearranges to the diazohydroxide. The diazoates are the salts of this diazohydroxide. The mechanism of changes may be represented as follows :

$$[C_6H_5-N\equiv N:]\overset{+}{}Cl \xrightarrow{NaOH} [C_6H_5-N\equiv N:]\overset{+}{}OH^-$$

Benzenediazonium chloride — Benzenediazonium hydroxide

$$C_6H_5\overset{+}{N}\equiv N: \longleftrightarrow C_6H_5-\ddot{N}=\overset{+}{N}: \overset{OH^-}{\rightleftharpoons} C_6H_5-\ddot{N}=\ddot{N}-OH$$

Benzenediazohydroxide

$$\xrightarrow{NaOH} [C_6H_5-\ddot{N}=\ddot{N}-\overset{-}{\ddot{O}}:]\overset{+}{Na}$$

Diazoate

6. Phenylhydrazine, $C_6H_5NH.NH_2$.

Preparation. Phenylhydrazine is prepared by the reduction of benzenediazonium chloride with acidified stannous chloride.

$$C_6H_5N_2Cl+4[H]\xrightarrow{SnCl_2/HCl}C_6H_5NH.NH_2.HCl \qquad (v.g.)$$

The reduction may also be carried out with sodium sulphite. Benzenediazonium chloride is poured into aqueous sodium sulphite. Concentrated hydrochloric acid is next added to the mixture which is then heated on a water-bath.

Properties. It is a colourless oily liquid (b.p. 514K) when freshly distilled but darkens on standing due to oxidation by air. It is very slightly soluble in water but very soluble in organic solvents. It has an unpleasant smell and is poisonous in nature. Various chemical reactions of phenylhydrazine are :

(*i*) *Basic nature.* It is strongly basic in character and forms well-defined salts such as phenylhydrazine hydrochloride,

$$C_6H_5NH.NH_2.HCl.$$

(*ii*) *Reducing action.* It is a powerful reducing agent and reduces Fehling's solution in the cold.

$$C_6H_5NH.NH_2 + 2Cu^{2+} + 4OH^- \longrightarrow C_6H_6 + Cu_2O + N_2 + 3H_2O$$

(*From Fehling's solution*) Red ppt

(*iii*) *Reduction.* On reduction with vigorous reducing agents (*e.g.*, Zn+HCl) it gives aniline and ammonia.

$$C_6H_5NH.NH_2+2[H]\xrightarrow{Zn/HCl}C_6H_5NH_2+NH_3$$

This reaction shows the structure of phenylhydrazine.

(*iv*) *Formation of Phenylhydrazones and Osazones.* With aldehydes and ketones it condenses to give phenylhydrazones while with sugars like glucose and fructose it gives osazones.

7. Diazoaminobenzene, $C_6H_5N{=}N.HNC_6H_5$.

Preparation. Diazoaminobenzene is formed when benzenediazonium chloride reacts with aniline in weakly acidic solution.

$$C_6H_5N_2\underline{Cl + H}NH.C_6H_5 \longrightarrow C_6H_5N{=}N.NH.C_6H_5+HCl$$

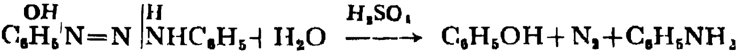
It may be prepared by treating aniline hydrochloride with calculated quantity of sodium nitrite just sufficient to diazotise half of the aniline and then adding sodium acetate.

$$C_6H_5N_2|\underline{Cl + H}\,NHC_6H_5+CH_3COONa \longrightarrow$$
$$C_6H_5N{=}N.NHC_6H_5+NaCl+CH_3COOH \qquad (v.g.)$$

Properties. It exists in two forms—golden-yellow prisms (m.p. 371K) and yellow prisms (m.p. 353K). It is insoluble in water but soluble in ethanol and ether. It explodes when heated rapidly. Its various chemical properties are :

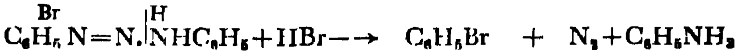
(*i*) *Basic Nature.* It is feebly basic in character and does not form stable salts with acids.

(*ii*) *Hydrolysis.* On boiling with dilute sulphuric acid it liberates nitrogen and forms phenol and aniline.



$$\overset{OH}{C_6H_5}|N{=}N|\overset{H}{N}HC_6H_5+H_2O \xrightarrow{H_2SO_4} C_6H_5OH+N_2+C_6H_5NH_2$$

(*iii*) *With Conc. HBr.* On boiling with concentrated hydrobromic acid it gives bromobenzene and aniline.

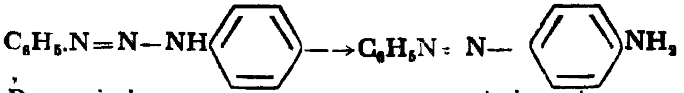


$$\overset{Br}{C_6H_5}\,N{=}N.|\overset{H}{N}HC_6H_5+HBr \longrightarrow \underset{\text{Bromobenzene}}{C_6H_5Br} + N_2+\underset{\text{Aniline}}{C_6H_5NH_2}$$

(*iv*) *With $NaNO_2$ and HCl.* With sodium nitrite and hydrochloric acid it gives benzenediazonium chloride.

$$C_6H_5N{=}N.NHC_6H_5+HNO_2+2HCl \longrightarrow 2C_6H_5N_2Cl+2H_2O$$

(*v*) *Rearrangement.* On warming diazoaminobenzene at 300-310K with a small amount of aniline hydrochloride (*catalyst*) or when the precipitate is left in contact with the mother liquor for several days it gives *p*-aminoazobenzene.



Diazoaminobenzene *p*-Aminoazobenzene

8. Dyeing and Calico-printing.—To ensure fastness, azo-dyes, highly insoluble in water, are directly produced on the fabric by coupling. The cloth to be dyed is soaked in an alkaline solution of a phenol, *e.g.*, β-naphthol, and dried. It is next immersed in an ice-cold solution of a diazonium salt when coupling takes place and an azo-dye is deposited within the pores of the fabric. The azo-dye being highly insoluble in water, the colour is fast to washing.

For **Calico printing**, β-naphthol is made into a paste with starch, gum, albumen, casein or glue. The desired design is printed on the cloth with this paste with the help of a hand block or an engraved cylinder and dried. It is next immersed in an ice-cold solution of a diazonium salt when the desired pattern or design is obtained in beautiful colours.

9. Aliphatic Diazo Compounds.—The aliphatic diazo compounds are characterised by the presence of the group $>CN_2$. Aliphatic amines cannot be diazotised like the aromatic amines but the esters of aliphatic amino-acids can be converted into diazo-esters by treating them with sodium nitrite and hydrochloric acid in aqueous solution. These are highly reactive compounds.

10. Diazomethane, CH_2N_2.

Preparation. Methylamine is treated with ethyl chloroformate to give *N*-methylurethan. This is treated with nitrous acid in ethereal solution when we get *N*-methyl-*N*-nitroso-urethan which on warming with methanolic KOH gives diazomethane. This is collected in cooled ether.

$$\underset{\text{Methylamine}}{CH_3NH_2} \xrightarrow{Cl.COOC_2H_5} \underset{N\text{-methylurethan}}{CH_3NH.COOC_2H_5} \xrightarrow{HONO}$$

$$\underset{\substack{N\text{-methyl-}N\text{-nitroso-}\\ \text{urethan}}}{CH_3N(NO)COOC_2H_5} \xrightarrow{KOH} \underset{\substack{\text{Diazo-}\\ \text{methane}}}{CH_2N_2} + CO_2 + C_2H_5OH$$

Properties. It is a yellow gas poisonous in nature, soluble in ether. Liquid diazomethane (b.p. 249K) is explosive in nature but the ethereal solution is fairly safe to handle. Reactions with diazomethane are, therefore, usually carried out in ethereal solution. It is an important methylating agent. Various chemical reactions of diazomethane are :

REACTIONS IN WHICH N_2 IS LOST :

With substances containing an active H-atom. Nucleophilic attack by diazomethane on compounds containing active hydrogen converts CH_2 into $—CH_3$ with evolution of N_2 gas.

(*i*) ***With halogen acids.***

$$CH_2N_2 + HCl \longrightarrow CH_3Cl + N_2$$

(*ii*) ***With acidic hydroxyl group*** (*e.g.*, —COOH, $—SO_2.OH$, phenols and enols).

$$RCOOH + CH_2N_2 \longrightarrow \underset{\text{Ester}}{RCOOCH_3} + N_2$$

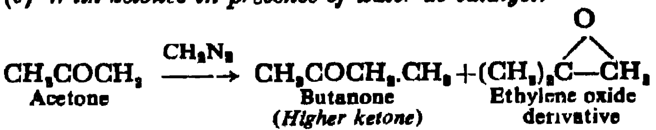
(*iii*) ***With alcohols in presence of aluminium alkoxide (catalyst).***

$$ROH + CH_2N_2 \xrightarrow{Al(OR')_3} \underset{\text{Ether}}{ROCH_3} + N_2$$

(*iv*) ***With aldehydes.***

$$RCHO + CH_2N_2 \longrightarrow RCOCH_3 + N_2$$

(*v*) ***With ketones in presence of water as catalyst.***



(*vi*) ***With amines.***

$$\underset{\substack{\text{Primary}\\\text{amine}}}{RNH_2} + CH_2N_2 \longrightarrow \underset{\textit{sec. }\text{amine}}{RNH.CH_3} + N_2$$

(*vii*) ***With amides.***

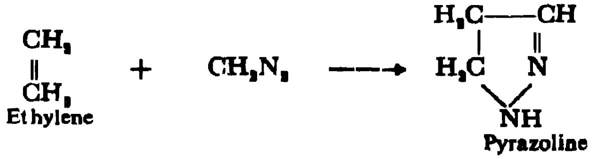
$$RCONH_2 + CH_2N_2 \longrightarrow \underset{N\text{-methylamide}}{RCONH.CH_3} + N_2$$

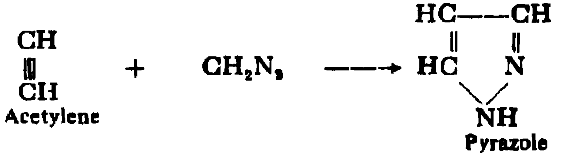
REACTIONS IN WHICH N_2 IS RETAINED :

(*i*) ***Reduction.*** It is reduced by sodium amalgam to methylhydrazine.

$$CH_2N_2 + 4H \xrightarrow{Na/Hg} \underset{\text{Methylhydrazine}}{CH_3NH.NH_2}$$

(*ii*) ***With alkenes and alkynes.*** With ethylene it forms an addition compound pyrazoline while with acetylene it gives pyrazole.





Diazomethane is best represented as a resonance hybrid of the following resonating structures :

$$\underset{(I)}{CH_2=\overset{+}{N}=\overset{-}{\ddot{N}}:} \longleftrightarrow \underset{(II)}{\overset{+}{C}H_2-\ddot{N}=\overset{-}{\ddot{N}}:} \longleftrightarrow \underset{(III)}{\overset{-}{\ddot{C}}H_2-\overset{+}{N}\equiv N:} \longleftrightarrow \overset{-}{\dot{C}}H_2-\ddot{N}=\overset{+}{N}:$$

Under appropriate conditions, diazomethane can act as an electrophile (II) or a nucleophile (III), as a 1, 3-dipole (IV), or as a source of methylene (see page 2·34).

11. Diazoacetic ester, Ethyl diazoacetate, $CHN_2COOC_2H_5$.

Preparation. Diazoacetic ester is conveniently prepared by treating a cooled solution of the hydrochloride of ethylglycine with a cold solution of sodium nitrite.

$$Cl^-H_3\overset{+}{N}—CH_2.COOC_2H_5+NaNO_2 \rightarrow N_2CH.COOC_2H_5+NaCl+2H_2O$$

Ethyl glycine hydrochloride — Diazoacetic ester

Properties. It is a yellow oil (b.p. 414K) insoluble in water but soluble in alcohol and ether. Its reactions given below are similar to those of diazomethane.

REACTIONS IN WHICH N_2 IS LOST :

(*i*) ***When boiled with dilute halogen acid, glycollic ester is produced.***

$$N_2CH.COOC_2H_5+H_2O \xrightarrow[\text{HCl}]{\text{Dil.}} CH_2OH.COOC_2H_5+N_2$$

Ethyl glycollate

(*ii*) ***With concentrated halogen acid, ethyl halogeno-acetate is produced.***

$$N_2CH.COOC_2H_5+HCl \longrightarrow CH_2ClCOOC_2H_5 + N_2$$

Ethyl chloroacetate

(*iii*) ***With compounds containing an active hydrogen atom, e.g.,*** acetic acid and ethanol.

$$CH_3COOH+N_2CHCOOC_2H_5 \longrightarrow CH_3CO.OCH_2COOC_2H_5+N_2$$

Acetic acid — Acetylglycollic ester

$$C_2H_5OH + N_2CHCOOC_2H_5 \longrightarrow C_2H_5O.CH_2COOC_2H_5 + N_2$$

Ethanol — Ethyl ether of glycollic ester

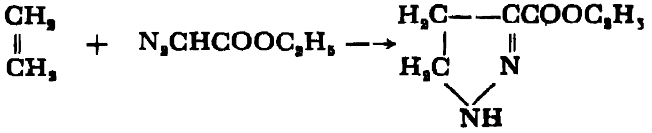
(*iv*) ***With iodine.***

$$N_2CHCOOC_2H_5+I_2 \longrightarrow CHI_2.COOC_2H_5+N_2$$

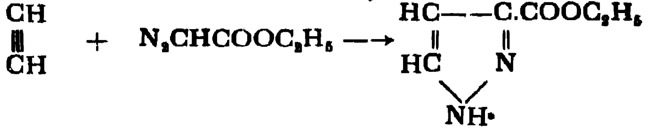
Ethyl diiodoacetate

REACTIONS IN WHICH N_2 IS RETAINED :

(*i*) ***Formation of heterocyclic compounds with ethylenic and acetylenic compounds.***



Pyrazoline-3-carboxylic ester



Pyrazole-3-carboxylic ester

(*ii*) ***Reduction.*** On reduction with zinc and acetic acid, it gives glycine ester and ammonia.

$$N_2CHCOOC_2H_5 \xrightarrow{4H} H_2N.CH_2COOC_2H_5+NH_3$$

Glycine ester

QUESTIONS

Essay Type :

1. (*a*) What is diazotisation ? How is benzenediazonium chloride prepared ? Describe its synthetic use.
(*Calicut B.Sc. 1974 ; Kamraj 1981 ; Jabalpur 1973 ; Marathwada 1972*)

(*b*) How and under what conditions does benzenediazonium chloride react with (*i*) *aniline*, (*ii*) *phenol* ? (*Bangalore B.Sc. 1974*)

2. How is benzenediazonium chloride prepared in solution ? What is its reaction with—

(*a*) dimethylaniline in a neutral aqueous solution ; (*b*) alkaline sodium stannite solution ; (*c*) stannous chloride dissolved in conc. HCl ; (*d*) potassium oxdide ; (*e*) cuprous bromide and HBr ; (*f*) alkaline solution of phenol ; and (*g*) β-naphthol dissolved in NaOH ? (*Jammu B.Sc. 1977*)

3. How is phenylhydrazine prepared ? Describe its important properties and uses

4. Describe the laboratory method for preparation of Benzenediazonium chloride. How will you prepare the following compounds from it :

(*a*) Chlorobenzene ; (*b*) Phenol ; (*c*) Benzoic acid ; (*d*) Benzene ; (*e*) Nitrobenzene ; (*f*) Iodobenzene ; (*g*) Phenetole ; and (*h*) *p*-Hydroxyazobenzene ? (*Kamraj B.Sc. 1981* ; *Delhi 1972* ; *Punjab T.D.C. I, 1971*)

5. Give the preparation, properties and uses of diazo-acetic ester.

6. By use of a diazo reaction as one step in the process show how you would prepare :

(*i*) Toluene from *o*-dinitrotoluene. (*ii*) 2 : 4 : 6-Tribromophenol from aniline. (*iii*) 3-Chloro-methoxybenzene from *m*-dinitrobenzene. (*iv*) *m*-Dichlorobenzene from benzene. (*v*) *p*-Toluic acid from *p*-toluidine. (*vi*) *m*-Hydroxybenzaldehyde from benzaldehyde, (*vii*) *p*-Dichlorobenzene from benzene. (*viii*) *p*-Bromophenol (*ix*) *m*-Bromochlorobenzene. (*x*) *p*-Chlorophenylacetic acid. (*xi*- 2 : 5-Dimethylphenol from *p*-xylene. (*xii*) *m*-Chlorophenylacetic acid.

Short Answer Type :

1. What is diazotisation ? Discuss its mechanism ? (*Delhi B.Sc. Hons. 1977* ; *Nagpur B.Sc. 1974 Supp.*)

2. How does a diazonium salt differ from a diazo compound ? (*Delhi B.Sc. Hons. 1977, 76*)

3. Describe briefly how the diazotisation of aniline is carried out. (*Delhi B.Sc. Hons. 1976*)

4. By using diazo reaction as one of the steps in the process, show how you would obtain the following from aniline :

(*a*) (*i*) 1, 3, 5-tri-bromobenzene ; (*ii*) phenol ;
(*iii*) *p*-hydroxy-azobenzene. (*Delhi B.Sc. Hons. 1976*)

(*b*) (*i*) phenylhydrazine, (*ii*) Methoxybenzene
(*iii*) Diazoaminobenzene. (*Nagpur B.Sc. 1974 Supp.*)

5. Write a short note on synthetic uses of diazonium compounds. (*Delhi B.Sc. 1976 Supp.*)

6 Excess of mineral acid is used in diazotisation process. Suggest reasons.

7 Benzenediazonium chloride couples with phenol but not with anisole. Explain why.

8. 2, 4-Dinitrobenzenediazonium chloride couples with methoxybenzene and 2, 4, 6-Trinitrobenzenediazonium chloride couples even with mesitylene. Give reasons.

9. Would you expect *p*-toluenediazonium chloride to be more or less reactive as a coupling reagent than benzenediazonium chloride ?

10. Outline the synthesis from benzene or toluene of the following compounds : (*i*) *m*-nitrotoluene, *m*-iodotoluene, 3, 5-dibromotoluene, 1,3,5-tribromobenzene, the three toluic acids and the three methylphenols.

(*ii*) *m*-dibromobenzene, *m*-iodonitrobenzene and *m*-fluoroaniline.

11. Write equations for the reaction of *p*-nitrobenzenediazonium chloride with : (*i*) *m*-phenylenediamine, (*ii*) hot dilute H_2SO_4, (*iii*) HBr+Cu, (*iv*) *p*-methylphenol (*v*) KI, (*vi*) CuCl, (*vii*) CuCN, (*viii*) HBF_4, then heat, (*ix*) H_3PO_2

12. How can you prepare the following compounds ?

(*i*) *m*-Nitroaniline (*ii*) *m*-Chloroaniline

(*iii*) *o*-Nitroaniline (*iv*) 1,3-Benzenediamine

(*v*) *p*-Nitroaniline (*vi*) *m*-Bromoaniline

13. Starting from *p*-toluidine how can you prepare : (*a*) *m*-Bromotoluene and (*b*) 3,5-Dibromotoluene ?

14. How will you prepare *o*- and *p*-bromotoluene beginning with toluene by a method other than direct bromination of toluene ?

15. How can you convert *p*-nitroaniline into 1, 2, 3-tribromobenzene ?

HINTS

12. (*i*) and (*iv*) Nitration of benzene at 370K followed by reduction with H_2S+NH_3 in (*i*) and Sn+HCl in (*iv*).

(*ii*) and (*v*) *m*-Nitroaniline obtained in (*i*) on diazotisation and the treatment with CuCl in (*ii*) and CuBr in (*vi*) followed by reduction of nitro group to NH_2.

(*iii*) and (*v*) Aniline on acetylation followed by nitration gives *o*- and *p*-nitroacetanilide which is hydrolysed and separated

13. (*a*) (*i*) Acetylation followed by bromination and then hydrolysis.

(*ii*) Diazotisation followed by reduction with H_3PO_2.

(*b*) Bromination followed by diazatisation and then H_3PO_2.

14. Nitration—reduction—diazotisation—CuBr.

15. Bromination—diazotisation followed by CuBr—reduction with Fe/HCl followed by diazotisation followed by H_3PO_2.

Problems :

1. An organic compound A has the molecular formula $C_6H_4O_4N_2$. On reduction with tin and hydrochloric acid it gives $C_6H_8N_2$ (B). On reduction with $(NH_4)_2S$, A gives $C_6H_6O_2N_2$ (C) which on diazotisation followed by treatment with cuprous chloride gives $C_6H_4O_2NCl$ (D). On reduction with tin and hydrochloric acid followed by diazotisation D gives $C_6H_4N_2Cl_2$ (E) which on treatment with methanol gives mainly C_7H_7OCl (F). Identify the compound A to F.

2. On nitration acetanilide gives two isomeric compounds A and B having molecular formula $C_8H_8O_3N_2$. A on reduction with tin and hydrochloric acid gives $C_6H_8N_2$ (C) which on diazotisation followed by treatment with CuCN gives $C_8H_4N_2$ (D). On hydrolysis D gives terephthalic acid.

B on hydrolysis followed by diazotisation yields $C_6H_4O_2N_3Cl$ (E) which on treatment with CuCl gives $C_6H_4O_2NCl$ (F). On reduction F gives chloroaniline (G). Identify the compounds A to G.

3. An organic compound A with mol. wt.=251 contains 63·7% of bromine. On diazotisation followed by reduction it gives a solid substance B containing 67·8% of bromine. B can give only one mono-nitro derivative.

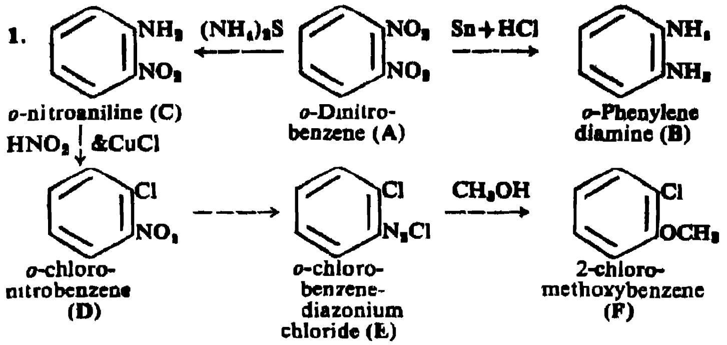
Another compound C is an isomer of A. It gives on diazotisation followed by treatment with CuBr a compound D containing 76·4% of bromine. D can give only one mono-nitro derivative.

Give the names and formulae of the compounds A and C

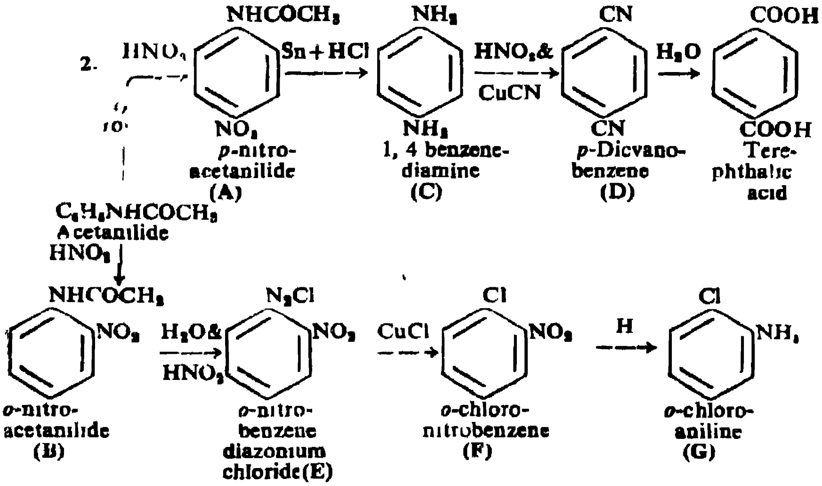
4. A neutral compound (A) with molecular formula $C_{10}H_{13}O_2N$ on reduction gives an amine (B) of the molecular formula $C_{10}H_{15}N$. B on diazotisation followed by reduction with Na_2SnO_2 yields a hydrocarbon $C_{10}H_{14}$ (C). On oxidation C gives a dibasic acid D. Both C and D can give only one mononitro derivative. Find the structural formula of A.

ANSWERS

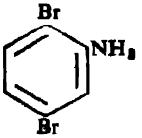
1.



2.

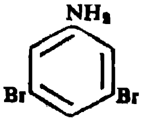


3. A is



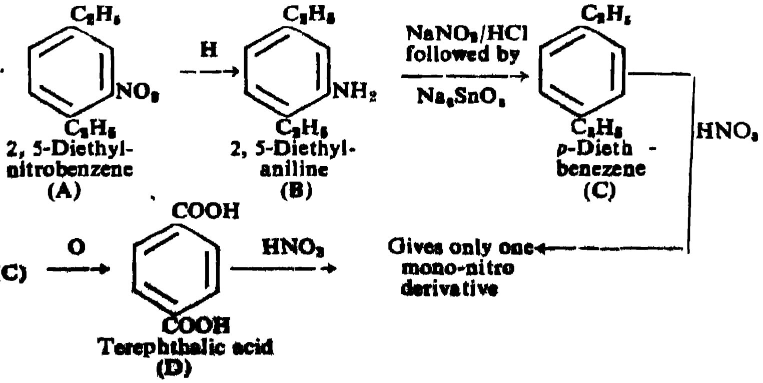
(2 : 5-Dibromoaniline)

C is



(3 : 5-Dibromoaniline)

4.

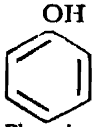


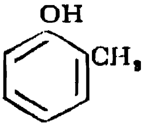
42

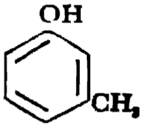
Phenols and Aromatic Alcohols

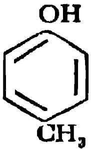
1. **Introductory.**—There are two types of aromatic hydroxy compounds :

(*i*) Those containing hydroxyl group directly attached to the nucleus are called *phenols*. These are further classified as monohydric, dihydric or trihydric phenols according as they contain one, two or three hydroxyl groups.

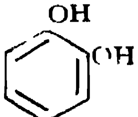

Phenol
or Benzenol

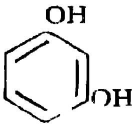

2-Methylphenol
or 2-Methylbenzenol

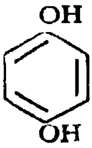

3-Methylphenol
or 3-Methylbenzenol


4-Methplphenol
or 4-Methylbenzenol

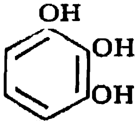
MONOHYDRIC PHENOLS

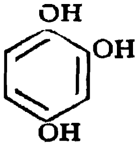

1, 2-Benzenediol

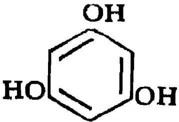

1, 3-Benzenediol


1, 4-Benzenediol

DIHYDRIC PHENOLS

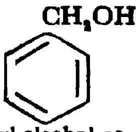

1, 2, 3-Benzenetriol

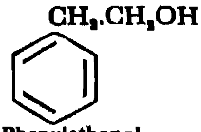

1, 2, 4-Benzenetriol


1, 3, 5-Benzenetriol

TRIHYDRIC PHENOLS

(*ii*) Those containing the hydroxyl group in the side-chain are termed *aromatic alcohols*. These may be regarded as aryl derivatives of the aliphatic alcohols. For example,


Benzyl alcohol *or*
Phenyl methanol


2 Phenylethanol
or Benzylmethanol

AROMATIC ALCOHOLS

2 General Methods of Preparation of Monohydric Phenols.

(*i*) *From coal-tar.* A number of monohydric phenols occur in coal-tar and are extracted from it. For example, *Middle oil* fraction of coal-tar contains phenols, methylphenols and dimethylphenols whereas *Heavy oil* contains methylphenols and higher phenols.

(*ii*) *By fusing sodium arenesulphonate with sodium hydroxide.*

$$\underset{\text{Sod. arenesulphonate}}{ArSO_3Na} + NaOH \longrightarrow \underset{\text{A phenol}}{ArOH} + Na_2SO_3$$

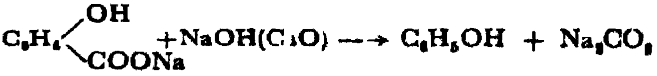
$$\underset{\text{Sod. benzenesulphonate}}{C_6H_5\overline{SO_3\,Na + Na}OH} \longrightarrow \underset{\text{Phenol}}{C_6H_5OH} + Na_2SO_3$$

(*iii*) *By steam distilling an aqueous solution of diazonium sulphate or chloride.*

$$\underset{\text{Diazonium sulphate}}{ArN_2HSO_4} + H_2O \longrightarrow \underset{\text{Phenol}}{ArOH} + N_2 + H_2SO_4$$

$$C_6H_5\boxed{N_2Cl + H}OH \longrightarrow C_6H_5OH + N_2 + HCl$$

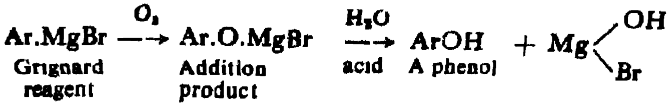
(*iv*) *By distilling a phenolic acid with soda-lime* (*Decarboxylation*).



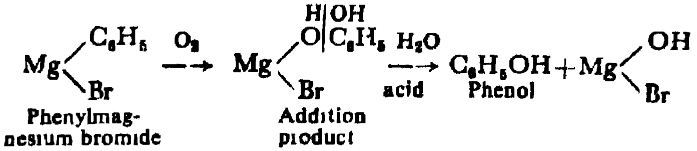
$$C_6H_4\begin{cases}OH\\COONa\end{cases} + NaOH(CaO) \longrightarrow C_6H_5OH + Na_2CO_3$$

Sodium salt of
o-, *m*- or *p*-hydroxybenzoic acid

(*v*) *From arylmagnesium halides* (*Grignard reagent*).

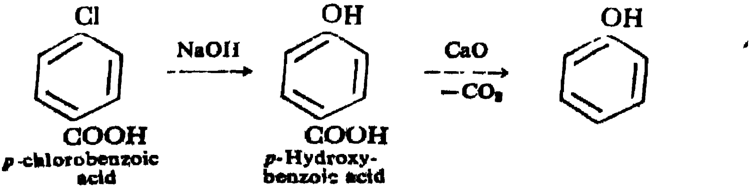


$$\underset{\substack{\text{Grignard}\\\text{reagent}}}{Ar.MgBr} \xrightarrow{O_2} \underset{\substack{\text{Addition}\\\text{product}}}{Ar.O.MgBr} \xrightarrow[\text{acid}]{H_2O} \underset{\text{A phenol}}{ArOH} + Mg\begin{cases}OH\\Br\end{cases}$$



$$\underset{\substack{\text{Phenylmag-}\\\text{nesium bromide}}}{Mg\begin{cases}C_6H_5\\Br\end{cases}} \xrightarrow{O_2} \underset{\substack{\text{Addition}\\\text{product}}}{Mg\begin{cases}O|C_6H_5\\Br\end{cases}} \xrightarrow[\text{acid}]{H_2O} \underset{\text{Phenol}}{C_6H_5OH} + Mg\begin{cases}OH\\Br\end{cases}$$

(*vi*) *By heating a compound containing an activated halogen atom with aqueous caustic soda.* For example, phenol is prepared by treating *p*-chlorobenzoic acid (in which chlorine atom is activated by the presence of COOH group in *p*-position) with aqueous sodium hydroxide followed by decarboxylation with soda-lime.



p-chlorobenzoic acid

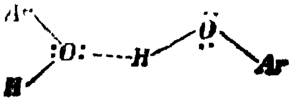
p-Hydroxybenzoic acid

3. General Properties of Monohydric Phenols.

Physical. Phenols are colourless crystalline solids or liquids although as usually encountered they are coloured red by oxidation products. They possess characteristic odours and are sparingly soluble in water but readily soluble in alcohol and ether. They are all toxic in nature and possess antiseptic properties.

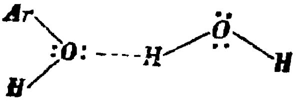
Compared to the boiling points of hydrocarbons of roughly the same molecular mass, phenols boil at much higher temperatures. For example, boiling point of C_6H_5OH (mol mass=94) is 453K compared to that of $C_6H_5CH_3$ (mol mass=92) being 383·6 K.

We can account for this contrast on the basis of strong hydrogen bonds present in phenol and their absence in hydrocarbons.



Association of phenols due to hydrogen bonding.

Appreciable water solubilities of phenols are also due to formation of strong hydrogen bonds between phenol and water molecules.



Hydrogen bonding between phenol and water molecules.

Chemical Benzenol or phenol is a typical member of monohydric phenols. Chemical properties of phenol are the general properties of phenols.

INDIVIDUAL MEMBERS

4. Phenol (Carbolic acid, Benzenol), C_6H_5OH.

Preparation. Different methods for the preparation of phenol are the general methods for the preparation of phenols described above. Any of these methods can be used for the preparation of phenol.

Manufacture. Phenol is prepared on a commercial scale :

(a) *By fusing sodium benzenesulphonate with caustic soda.* This is the oldest synthetic method for the manufacture of phenol.

$$C_6H_5SO_3Na \xrightarrow{NaOH} C_6H_5ONa \xrightarrow{HCl} C_6H_5OH$$

(b) *By heating chlorobenzene under pressure with 10 per cent solution of sodium carbonate or sodium hydroxide at about 570K in presence of copper salts (catalyst).*

$$\text{(i)}\ C_6H_5|Cl + Na|OH \xrightarrow[200\ \text{atm.}]{570K} \underset{\text{Phenol}}{C_6H_5OH} + NaCl$$

$$(ii)\quad C_6H_5Cl + C_6H_5OH + NaOH \longrightarrow \underset{\text{Diphenyl ether}}{(C_6H_5)_2O} + NaCl + H_2O$$

Diphenyl ether (about 10%) is, therefore, added to the reaction mixture to prevent the reaction (*ii*) above.

(*c*) One of the latest methods for the synthetic preparation of phenol on an industrial scale is by *heating chlorobenzene* (obtained by *Raschig method, page 2 518*) *with steam at 700K in the presence of a catalyst*

$$2C_6H_6 + 2HCl + O_2 \xrightarrow{CuCl_2} 2C_6H_5Cl + 2H_2O$$

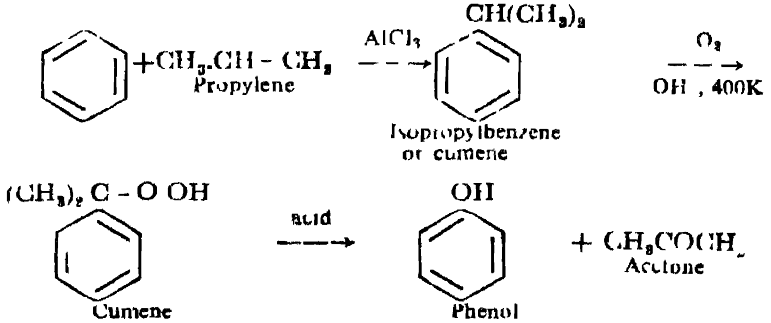
$$\underset{\text{Chlorobenzene}}{C_6H_5Cl} + H_2O \longrightarrow \underset{\text{Phenol}}{C_6H_5OH} + HCl$$

The hydrochloric acid produced in the second reaction is used in the first

(*d*) Another new method for the synthetic preparation of phenol is to pass a mixture of benzene and air over vanadium pentoxide at 580K when benzene is directly oxidised to phenol

$$2C_6H_6 + O_2 \longrightarrow 2C_6H_5OH$$

(*e*) *By oxidation of cumene followed by treatment with acid* This is also one of the latest methods used for the manufacture of phenol



(*f*) *From coal-tar* The middle oil fraction of coal tar (440-500K) is allowed to stand when naphthalene crystallizes out This is separated in the centrifuge The oily layer is washed with dilute sulphuric acid to remove basic impurities like pyridine and then treated with excess of ten per cent sodium hydroxide when phenol passes into solution as sodium phenoxide.

The aqueous layer is separated from the oily impurities and acidified with sulphuric acid or carbon dioxide is passed through, thereby decomposing the sodium phenoxide into free phenol Phenol liberated as an oily liquid is washed with water and subjected to fractional distillation The fraction distilling between 453 and 456K is pure phenol. On cooling phenol gives colourless crystals which are separated from any methylphenols present (still liquid).

Properties : Physical. It is a colourless, crystalline substance (m.p. 316K ; b.p. 455K) moderately soluble in water, more in alcohol and ether. The needle-shaped crystals are hygroscopic, corrosive and poisonous. These turn pink on exposure to air and light.

Phenol is soluble in water to the extent of 29 g per 100 g of water at 298K. The two are, however, miscible at 338K. Water is soluble in phenol to the extent of 29 g per 100 g of phenol. Melting point of phenol (316K) is lowered by the presence of a small amount of water. Phenol containing 5% water is liquid at room temperature and is termed carbolic acid.

Chemical. Phenol contains one enolic alcoholic group, $\gg$COH and thus resembles aliphatic alcohols in many respects. The presence of benzene nucleus accounts for its properties different from those of alcohols.

A. Reactions similar to those of Alcohols.

(*i*) **With metallic sodium.** Phenol reacts with metallic sodium to give sodium phenoxide (*cf.*, **sodium alkoxide**).

$$\underset{\text{Phenol}}{2C_6H_5OH} + 2Na \longrightarrow \underset{\text{Sod. phenoxide}}{2C_6H_5ONa} + H_2$$

$$(cf.,\ 2C_2H_5OH + 2Na \longrightarrow \underset{\text{Sod. ethoxide}}{2C_2H_5ONa} + H_2)$$

(*ii*) **Alkylation.** Phenolic ethers are obtained by treating alkali phenoxide with alkyl halide or passing phenol vapours alone or mixed with some alcohol vapours over heated thoria.

$$\underset{\text{Pot phenoxide}}{C_6H_5O|K} + I|C_2H_5 \longrightarrow \underset{\text{Ethoxybenzene}}{C_6H_5OC_2H_5} + KI$$

$$(cf.,\ \underset{\text{Sod. ethoxide}}{C_2H_5O\underline{Na + I}}|C_2H_5 \longrightarrow \underset{\text{Ether}}{C_2H_5OC_2H_5} + NaI)$$

$$C_6H_5O|\underline{H + HO}|CH_3 \xrightarrow[\text{thoria}]{\text{Heated}} \underset{\text{Methoxybenzene}}{C_6H_5OCH_3} + H_2O$$

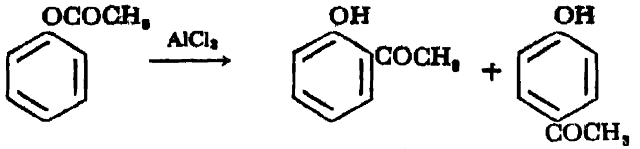
$$(cf.,\ C_2H_5O\ \underline{H + HO}|C_2H_5 \xrightarrow[\text{at 410K or heated } Al_2O_3]{\text{Conc. } H_2SO_4} \underset{\text{Diethyl ether}}{C_2H_5OC_2H_5} + H_2O)$$

(*iii*) **Acetylation.** With acetyl chloride or acetic anhydride H atom of the —OH group in phenol is replaced by —$COCH_3$ group.

$$C_6H_5O|\boxed{H + Cl}\,COCH_3 \longrightarrow \underset{\text{Phenyl acetate}}{C_6H_5O.COCH_3} + HCl$$

$$(cf.,\ C_3H_7O|\boxed{H + Cl}|COCH_3 \longrightarrow \underset{\text{Propyl acetate}}{C_3H_7O.COCH_3} + HCl)$$

The ester on treatment with anhydrous $AlCl_3$ undergoes **Fries rearrangement** *to give* *o*- or *p*-hydroxy ketone or a mixture of both.



o- and *p*-hydroxyacetophenone

At temperatures below 330K the *p*-isomer is obtained in larger yield whereas at temperatures above 430K, the *o*-isomer is obtained in larger yield.

(*iv*) **With phosphorus halides.** The hydroxyl group of phenols, unlike that of alcohols, is difficult to replace by halogen. For example, halogen acids have no action and phosphorus trihalides yield only phosphorous esters. Phenol reacts with phosphorus pentahalides (pentachloride or pentabromide) when the —OH group is replaced by a halogen atom. The yield of chloro- or bromobenzene is small and the main product is triphenyl phosphate $(C_6H_5O)_3PO$

$$\underset{\text{Phenol}}{C_6H_5OH} + PCl_5 \longrightarrow \underset{\text{Chlorobenzene}}{C_6H_5Cl} + POCl_3 + HCl$$

$$(cf.,\ CH_3OH + PCl_5 \longrightarrow CH_3Cl + POCl_3 + HCl)$$

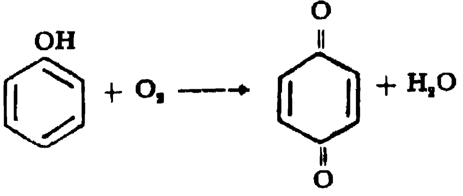
(*v*) **With Ammonia.** Phenol, when heated with ammonia in presence of anhydrous zinc or calcium chloride, gives aniline.

$$\underset{\text{Phenol}}{C_6H_5|OH} + \underset{\text{Ammonia}}{H|NH_2} \xrightarrow{ZnCl_2} \underset{\text{Aniline}}{C_6H_5NH_2} + H_2O$$

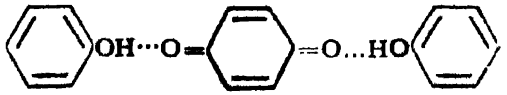
$$(cf.,\ C_2H_5|OH + H|NH_2 \xrightarrow[\text{thoria}]{\text{Heated}} \underset{\text{Ethylamine}}{C_2H_5NH_2} + H_2O)$$

Aniline is also obtained by heating phenol with ammonia under pressure.

(*vi*) **Oxidation.** Phenol turns pink on exposure to air and light due to slow oxidation. Complex mixtures of products are formed on oxidation by air or other oxidising agents. One of the oxidation products in air is quinone which forms a brilliant red addition product with phenol known as phenoquinone, in which two phenol molecules are joined to one molecule of quinone through hydrogen bonds.

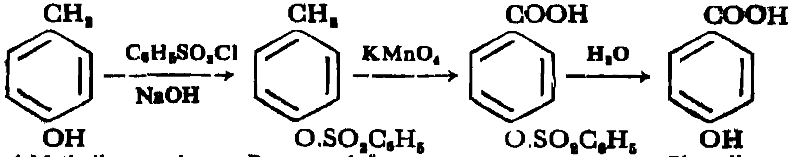


$$\underset{\text{Quinone}}{C_6H_4O_2} + 2C_6H_5OH \longrightarrow$$



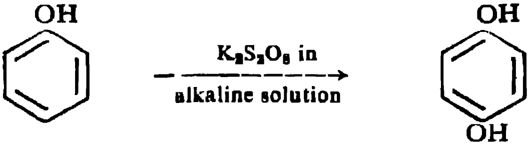
Phenoquinone

On oxidising phenol or its homologues with potassium permanganate the ring breaks. If, however, the phenolic group is protected by alkylation or acylation, homologues of phenol are oxidised to phenolic acids. For example,

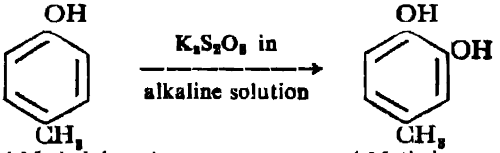


4-Methylbenzenol *or* 4-Methylphenol — Benzenesulphonate of 4-Methylphenol — Phenolic acid

Monohydric phenols on oxidation with potassium persulphate in alkaline solution yield dihydric phenols. The newly-entering —OH group enters *p*-position to the hydroxyl group. In case *p*-position is not free, the new group enters *o*-position to the hydroxyl group.



Phenol — 1, 4-Benzenediol



4-Methylphenol — 4-Methyl-1, 2-Benzenediol

This is known as **Elbs persulphate oxidation.**

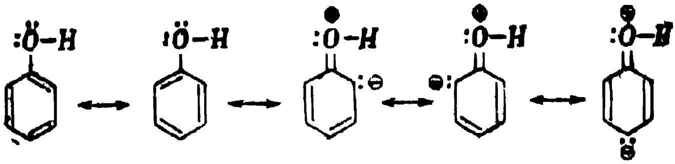
B. Reactions different from those of alcohols.

(*i*) **Acidic nature.** The —OH group behaves weakly acidic. With alkalis it gives phenoxides. Since phenol is a weaker acid it does not decompose carbonates.

$$C_6H_5OH + HONa \longrightarrow C_6H_5ONa + H_2O$$

Phenol — Sod. phenoxide

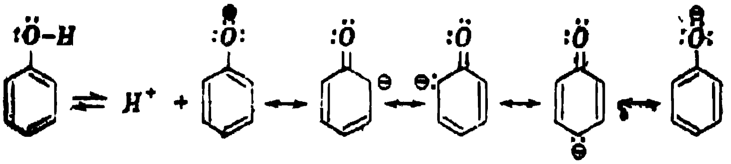
One possible explanation why phenols are stronger acids than the alcohols is that the phenols exist as a resonance hybrid.



(*i*) The oxygen atom gets a positive charge due to resonance and attracts the electron pair of the O—H bond and thus facilitates the release of a proton. Carbon atom of the >COH group in phenol being sp^2 hybridised is more electron-attracting than the

sp^3 carbon atom in alcohols. Thus in phenols there is greater −I effect which facilitates proton release. However, this effect is minor in comparison to the resonance effect given above.

(*ii*) The negative phenoxide ion formed after the release of a proton is at the same time stabilised by resonance.



Since no resonance is possible in alcohols, the hydrogen atom is more firmly linked to the oxygen.

Effect of substituents on acidity. The effect of ring substituent G depends on the following ;

(*i*) *Nature of G whether it is electron-attracting or electron-releasing.* Electron-attracting substituents tend to disperse the negative charge of the phenoxide ion, thus stabilize the ion and increase acidity. Electron-releasing substituents tend to intensify the charge and thus destabilize the ion and decrease acidity.

(*ii*) *Its ability to enter into resonance with the hydroxyl group.* Electron-releasing groups like CH_3 having strong +R effect oppose the release of the lone pair from oxygen (of OH group in the unionised phenol or O^- in the phenoxide ion) into the ring, resulting in diminished resonance, and reduced stability of methylphenoxide ion in comparison to that of phenoxide ion. Hence methylphenol is a weaker acid than phenol. *Thus in general, electron-releasing groups reduce the acidity of phenol by diminishing resonance.*

Electron-withdrawing groups like nitro, having —R effect, help the release of the lone pair from oxygen. This results in increased resonance in the contributing structures and greater stability of the phenoxide ion. Nitrophenol is, therefore, stronger acid than phenol. *In general, electron-withdrawing groups increase the acidity by increasing resonance.*

(*ii*) *Its position.* Since nitro group can enter into resonance with the hydroxyl group only from *o*- and *p*-positions, *o*- and *p*-nitrophenoxides are resonance stabilised, not the *m*-nitrophenoxide. Hence *o*- and *p*-nitrophenols are stronger acids than phenol. Picric acid (2, 4, 6-trinitrophenol) is a very strong acid (pK_a=0·71) due to the cumulative effect of three nitro groups in *o*- and *p*-positions.

There may be added complications due to steric effect and hydrogen bonding (when possible).

Acidity of various substituted phenols are given on the next page in terms of their pK_a values. Higher the pK_a value of a substituted phenol, lower its acidity, The pK_a value for unsubstituted phenol=9·98

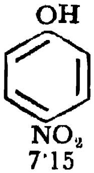
Substituent	pK_a *o-*	*m-*	*p-*
CH_3	10·28	10·08	10·14
NO_2	7·23	8·40	7·15
Cl	8·48	9·02	9·38
MeO	9·98	9·65	10·21
NH_3	9·71	9·87	10·30

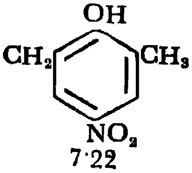
Relative strengths of various isomers can be explained in the light of above discussion. For example, *o-* and *p*-nitrophenols are stronger than *m*-nitrophenol which is stronger than phenol. This is because NO_2 in *o-* and *p*-positions exerts both $-R$ and $-I$ effect whereas in *m*-position it has only $-I$ effect.

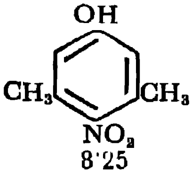
NH_2 and MeO groups when present in *p*-position exert $+R$ effect as well as $-I$ effect. But $+R$ effect being stronger than $-I$ effect, their presence in *p*-position decreases the acidity of phenol. But the *m*-derivatives are slightly stronger than phenol due to $-I$ effect alone (since it exerts no resonance effect in this position).

All halogenophenols are stronger acids than phenol. It shows that in their case $-I$ effect is stronger than $+R$ effect.

Effect of a certain group in *o*-position may be opposite to its effect in *p*-position due to hydrogen bonding (when possible) which stabilises the unionised form. The difference may also be due to steric effect. For example, in the following compounds







pK_a 7·15 7·22 8·25

I II III

decrease in acid strength from I to II is due to $+I$ effect of two *o*-methyl groups in II. A large decrease in acid strength from I to III is due to steric inhibition of resonance of NO_2 group with OH by two *o*-methyl groups.

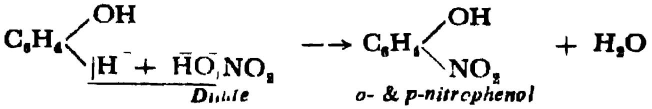
(*ii*) Reduction with Zinc dust. Phenol when heated with zinc dust gives benzene (*cf.*, aliphatic alcohols which are reduced to hydrocarbons with hydriodic acid).

$$C_6H_5OH + Zn \longrightarrow C_6H_6 + ZnO$$

Reduction may also be carried out with hydrogen at atmospheric pressure in presence of molybdenum oxide (*catalyst*).

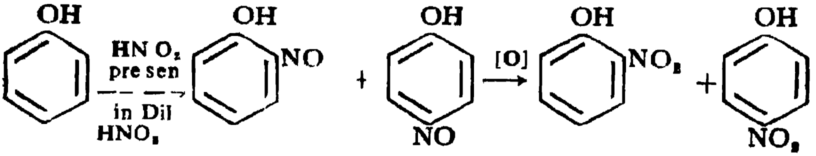
$$C_6H_5OH + H_2 \longrightarrow C_6H_6 + H_2O$$

(*iii*) **Nitration.** Presence of —OH group in the nucleus facilitates the substitution reactions (nitration, sulphonation and halogenation) and ortho- and para-derivatives are obtained in each case. For example, phenol is nitrated even with dilute nitric acid.



$$C_6H_4\Big\langle{}^{OH}_{H} + \underset{\text{Dilute}}{HO\,NO_2} \longrightarrow \underset{\text{o- \& p-nitrophenol}}{C_6H_4\Big\langle{}^{OH}_{NO_2}} + H_2O$$

It is believed that at first nitrosophenol is obtained. This is followed by oxidation of nitroso group by nitric acid.



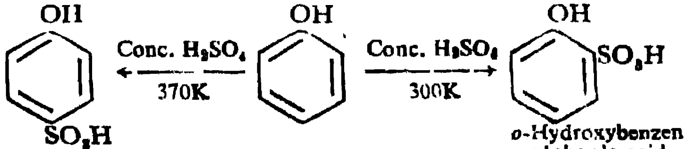
Phenol $\quad$ *o*- & *p*-nitrosophenols $\quad$ *o*- & *p*-nitrophenols

If urea is added to destroy nitrous acid present in nitric acid or formed by its reduction, no nitration takes place.

The two isomers can be separated by steam-distillation, since the ortho isomer is much more volatile.

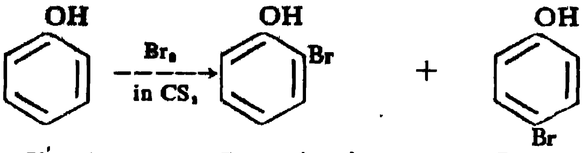
Nitration of phenol with concentrated nitric acid gives 2, 4, 6-trinitrophenol (picric acid) but the amount of oxidation is excessive. Picric acid is, therefore, prepared by an indirect method (*see* under picric acid).

(*iv*) **Sulphonation.** As stated above sulphonation takes place readily. At room temperature concentrated sulphuric acid yields chiefly the ortho isomers, whereas at 370K it gives mainly the para isomer.



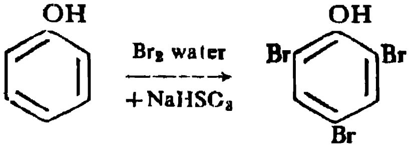
p-Hydroxybenzene-sulphonic acid $\quad$ Phenol $\quad$ *o*-Hydroxybenzene sulphonic acid

(*v*) **Halogenation.** Controlled halogenation of phenol in presence of anhydrous solvents at low temperatures gives monohalogen derivatives (mainly para derivative).



Phenol o-Bromophenol *p*-Bromophenol (80-84%)

Addition of bromine water to an aqueous solution of phenol containing some sodium bisulphite yields 2, 4, 6-tribromophenol.



2, 4, 6-Tribromophenol

Different products are obtained with Br_2 in CS_2 and Br_2 water. The reason for this difference is believed to be the nature of subtstrate in the two cases. In Br_2 water the substrate is phenoxide ion (produced by ionisation in water) which activates the ring more than phenol. The ionisation to give $C_6H_5O^-$ is not possible in phenol.

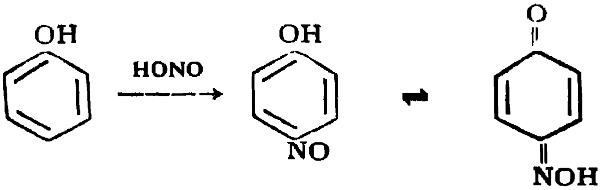
(*vi*) **Coloured complexes with Ferric chloride**. Enols [compounds containing the grouping —C(OH)=C<] in general give coloured water-soluble complexes with ferric chloride. The complexes are probably coordination compounds in which iron is hexacovalent. Different colours are obtained with different phenols as given below :

Phenol	*violet* ;	1, 3, 5-Benzenetriol	*dark violet* ;
1, 2, 3-Benzenetriol	*red* ;	1, 3-Benzenediol	*violet* ;
1, 4 Benzenediol	*transient blue* ;	1, 2- Benzenediol	*green*.

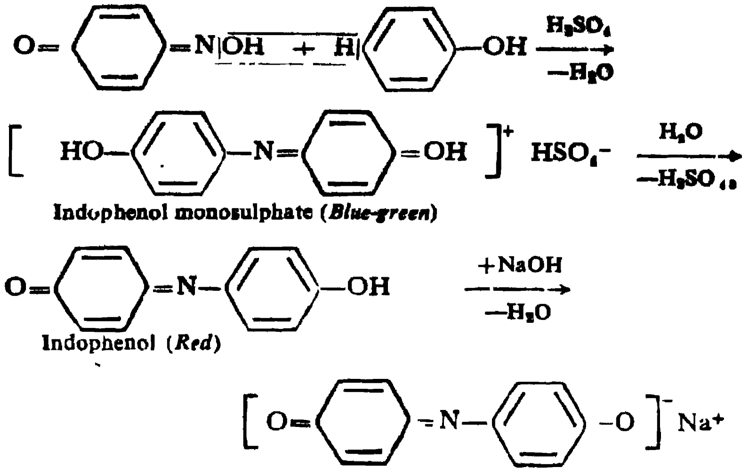
(*vii*) **Coupling**. Phenol couples in the *p*-position with diazonium salts in alkaline solution to form hydroxyazo compounds. (*see* page 2·581).

(*viii*) **Liebermann's Nitroso Reaction**. On warming with concentrated sulphuric acid and sodium nitrite, phenol gives a brown or red colour which soon changes to blue-green. The colour changes red when diluted largely and deep blue when treated with sodium hydroxide. Various reactions taking place are :

Phenol reacts with nitrous acid to give *p*-nitrosophenol which is tautomeric monoxime of quinone.



In the presence of conc. H_2SO_4 the monoxime condenses with phenol to give blue-green solution of indophenol monosulphate which on dilution gives indophenol (*red*). With excess of sodium hydroxide we get sodium salt of indophenol (*deep blue*).

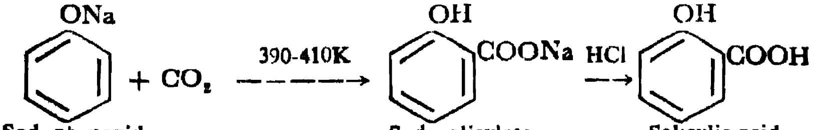


Indophenol monosulphate (*Blue-green*)

Indophenol (*Red*)

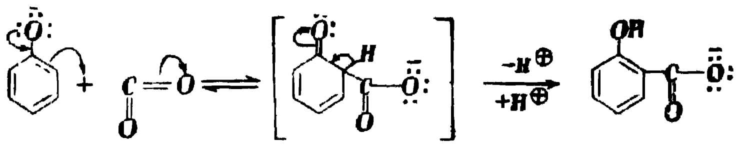
Sodium salt (*Deep blue*)

(*ix*) **Kolbe's Reaction.** At present a modification of Kolbe's reaction known as **Kolbe-Schmitt method** is used. Sodium phenoxide when heated (390-410K) under pressure with carbon dioxide, gives salicylic acid.



Sod. phenoxide Sod. salicylate Salicylic acid

The mechanism of the reaction is uncertain ; a possibility is :

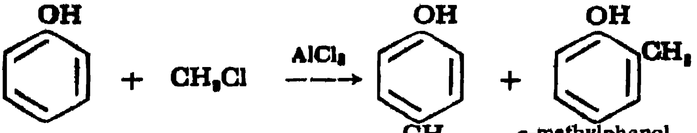


A small amount of the *p*-isomer is also obtained but *p*-isomer is the main product if the temperature rises above 430K, or when potassium phenoxide is used instead of sodium salt.

(*x*) **Hydrogenation.** Phenol on hydrogenation at 430K in the presence of a nickel catalyst gives *cyclohexanol*.

$$\underset{\text{Phenol}}{C_6H_5OH} + 3H_2 \xrightarrow{Ni} \underset{\text{Cyclohexanol}}{C_6H_{11}OH} \qquad (ex.)$$

(*xi*) **Friedel-Crafts Reaction.** Phenol undergoes the Friedel-Crafts reaction to form mainly the *p*-derivative with a small quantity of the *o*-isomer.

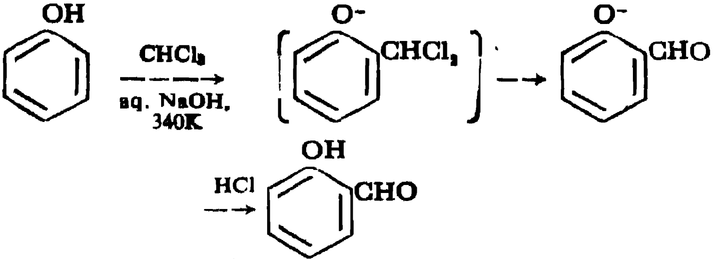


Phenol

p-methylphenol

o-methylphenol (*small quantity*)

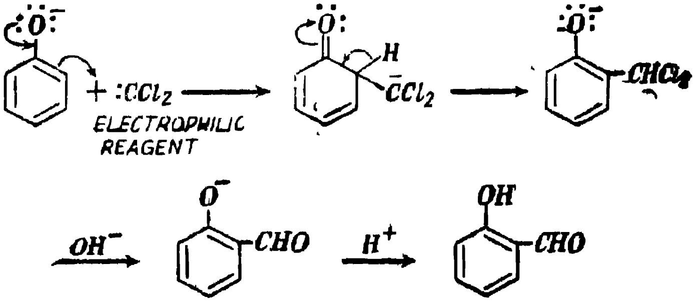
(*xii*) **Reimer-Tiemann Reaction.** When refluxed with chloroform and alkali, phenol yields *o*- and *p*-hydroxybenzaldehyde, the former predominating.



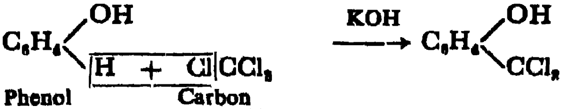
Salicylaldehyde
(*chief product*)

Reimer-Tiemann reaction involves electrophilic substitution on the highly reactive phenoxide ring. *The electrophile is dichloromethylene, $:CCl_2$, generated from chloroform by the action of base.* Although electrically neutral, dichloromethylene contains a carbon atom with only a sextet of electrons and hence is strongly electrophilic.

$$OH^- + CHCl_3 \rightleftharpoons H_2O + :\bar{C}Cl_3 \longrightarrow Cl^- + :CCl_2$$



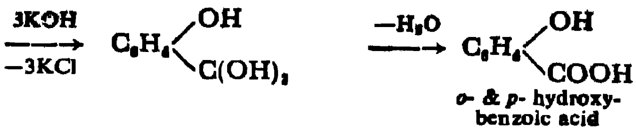
Similarly, with carbon tetrachloride and alkali *o*- and *p*-hydroxybenzoic acid is obtained.



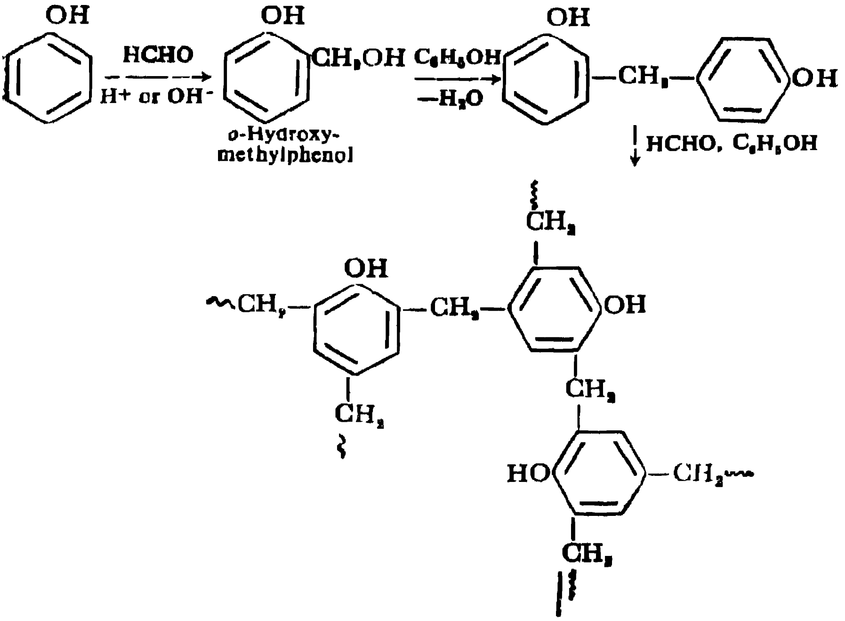
$$C_6H_4\begin{cases}OH\\ \boxed{H + Cl}CCl_3\end{cases} \xrightarrow{KOH} C_6H_4\begin{cases}OH\\ CCl_3\end{cases}$$

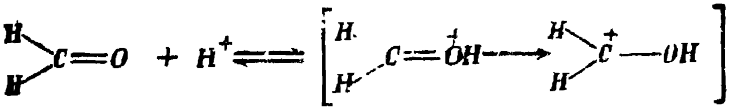
Phenol

Carbon tetrachloride

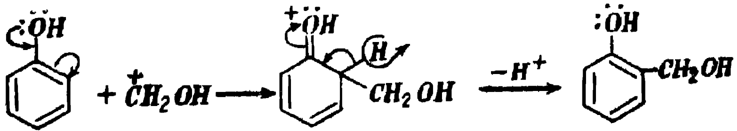


(*xiii*) **Condensation Reactions.** Phenol condenses with aliphatic and aromatic aldehydes in the *o*- and *p*-positions. For example, with formaldehyde in presence of dilute acid or alkali and a catalyst it yields bakelite (*a resin*).

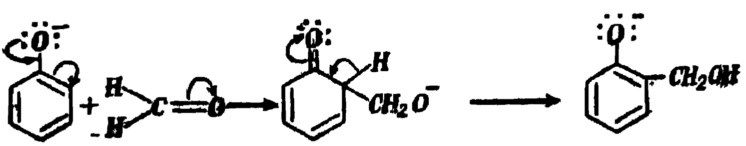




PROTONATED FORMALDEHYDE



ACID CATALYSIS



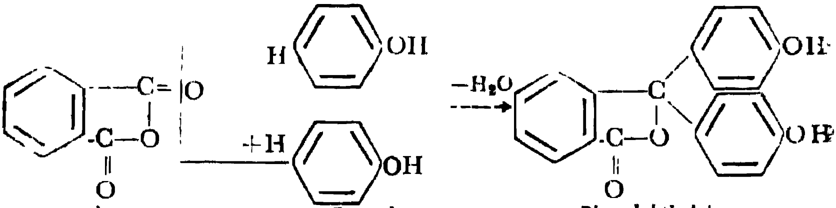
BASE CATALYSIS

In the first stage phenol reacts with formaldehyde to form *o*- or *p*-hydroxmethylphenol which reacts with another molecule of phenol with the loss of water to form a compound in which two rings are joined through a —CH_2— link. The process continues to form a three-dimensional polymer of high molecular weight.

The first stage is known as the **Lederer-Manasse reaction.** It can be viewed as electrophilic substitution on the ring by the electron-deficient carbon of formaldehyde. It can also be viewed as nucleophilic addition of the aromatic ring to the carbonyl group.

Base catalyses the reaction by converting phenol into more reactive (more nucleophilic) phenoxide ion. Acid catalyses the reaction by protonating formaldehyde and increasing the electron deficiency of the carbonyl carbon.

When heated with phthalic anhydride in presence of concentrated sulphuric acid, it yields phenolphthalein (gives pink colour with alkalis).



Phthalic anhydride *Phenol (Two molecules)* *Phenolphthalein*

Uses. Phenol is used :

(*i*) In the manufacture of drugs like salol, aspirin, salicylic acid and phenacetin.

(*ii*) As an antiseptic—carbolic lotion and carbolic soap.

(*iii*) For the manufacture of bakelite (a resin), picric acid (an explosive), phenolphthalein (an indicator) and other dyestuffs.

(*iv*) As a preservative for ink.

(*v*) For the manufacture of cyclohexanol used as solvent for rubber and lacquers.

Tests. (*i*) *Smell.* Phenol has a characteristic smell.

(*ii*) *Ferric chloride test.* With a drop of ferric chloride (neutral solution), phenol gives a violet coloration.

(*iii*) *With bromine water,* an aqueous solution of phenol gives white precipitate of tribromophenol.

(*iv*) *Phenolphthalein test.* On heating phenol with phthalic anhydride and a few drops of concentrated sulphuric acid, phenolphthalein is obtained. This gives a pink colour with an alkali.

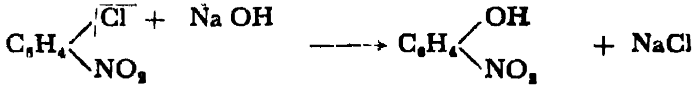
(*v*) It gives Liebermann's nitroso-reaction.

SUBSTITUTED PHENOLS

5. Nitrophenols.—*o*- and *p*-Nitrophenols are prepared—

(*i*) By direct nitration of phenol with dilute nitric acid. The two are separated by steam-distillation when the *o*-isomer distils over leaving the *p*-isomer behind.

(*ii*) By treating *o*- and *p*-chloronitrobenzene with aqueous sodium hydroxide

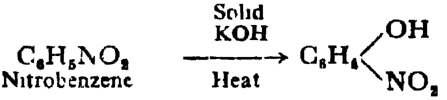


$$C_6H_4\begin{cases}Cl\\NO_2\end{cases} + NaOH \longrightarrow C_6H_4\begin{cases}OH\\NO_2\end{cases} + NaCl$$

o- and *p*-chloro-nitrobenzene

o- and *p*-nitro-phenol

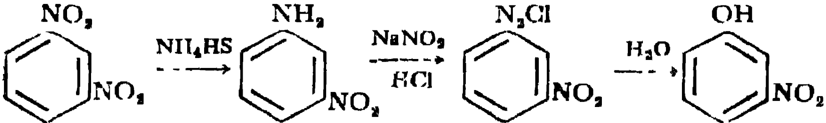
(*iii*) By heating nitrobenzene with solid potassium hydroxide



$$C_6H_5NO_2 \xrightarrow[\text{Heat}]{\text{Solid KOH}} C_6H_4\begin{cases}OH\\NO_2\end{cases}$$

Nitrobenzene

m nitrophenol is prepared from *m*-dinitrobenzene.



m-Dinitro-benzene

m-Nitro-aniline

m-Nitrobenzene-diazonium chloride

m-Nitro-phenol

Properties *o*-Nitrophenol is a yellow solid (m.p. 318K) while the *m*- and *p*-isomers are colourless solids (m.p. 370K and 387K respectively) These are all sparingly soluble in water. The *o*-isomer is volatile in steam. They are stronger acids than phenol The *o*- and *p* isomers are stronger acids than the *m*-isomer On reduction they give the corresponding amino-phenols On treatment with bromine water nitro group in the *o*- and *p*-derivatives is displaced and 2, 4, 6-tribromophenol is produced.

The salts of free nitrophenols are highly coloured (yellow to red)

From a comparison of the physical properties of isomeric nitrophenols in the following table we notice that *o*-nitrophenol has a much lower boiling point and much lower solubility in water than its isomers. It is volatile in steam unlike its meta and para isomers.

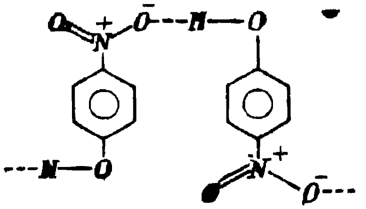
Table 42 2—Physical Properties of Nitrophenols

Isomer	B P (K) at 70 mm	Solubility g/100 g H$_2$O	Volatility in steam
ortho	373	0·2	Volatile
meta	467	1·35	Non-volatile
para	decomposes	1·69	Non-volatile

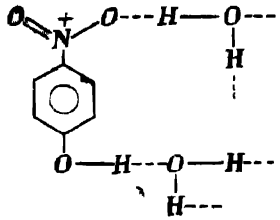
These differences are accounted for on the basis of differences in the nature of hydrogen bonding.

The *m*- and *p*-isomers have very high boiling points because of intermolecular hydrogen bonding while their solubility in water is due to hydrogen bonding with water molecules :

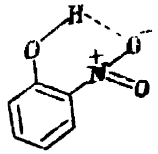
In *o*-isomer the $—NO_2$ and —OH groups being closer result in the formation of a hydrogen bond *within a single molecule*. This **intramolecular hydrogen bonding** takes the place of *intermolecular hydrogen bonding* with other phenol molecules and with water molecules.



Intermolecular
hydrogen bonding



Hydrogen bonding
with water molecules



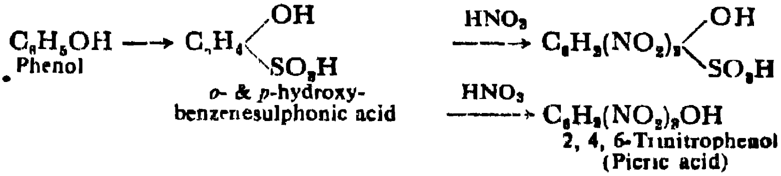
Intramolecular
hydrogen bonding
chelation

o-Nitrophenol

o-Nitrophenol, therefore, neither has the low volatility of an associated liquid, nor has the solubility characteristic of a compound that forms hydrogen bonds with water.

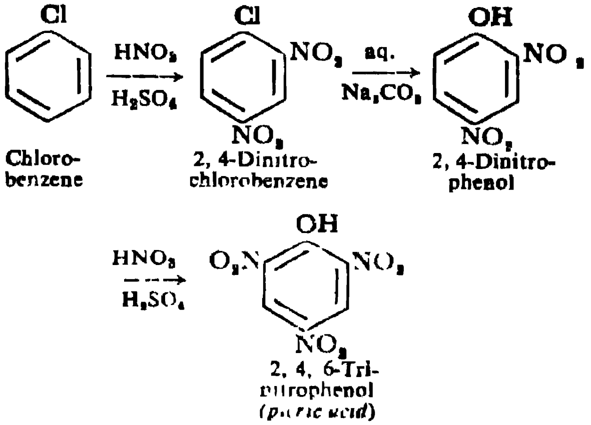
6. **Picric acid** (**2, 4, 6-trinitrophenol**), $C_6H_2(OH)(NO_2)_3$.—Picric acid is obtained when phenol is nitrated with concentrated nitric acid. The yield is, however, poor, due to losses by oxidation. It is prepared *on an industrial scale* :

(*i*) *By first sulphonating phenol and then nitrating the product* since the sulphonic acid derivative is not easily oxidised.

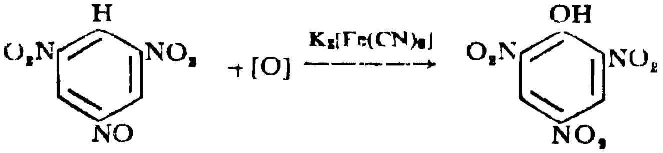


$$\underset{\text{Phenol}}{C_6H_5OH} \longrightarrow \underset{o\text{- \& }p\text{-hydroxybenzenesulphonic acid}}{C_6H_4\begin{cases}OH\\SO_3H\end{cases}} \xrightarrow{HNO_3} C_6H_2(NO_2)_2\begin{cases}OH\\SO_3H\end{cases} \xrightarrow{HNO_3} \underset{\text{2, 4, 6-Trinitrophenol (Picric acid)}}{C_6H_2(NO_2)_3OH}$$

(*ii*) *From chlorobenzene* as given below :



It may be prepared *in the laboratory* by oxidising *s*-trinitrobenzene with potassium ferricyanide :



Properties Picric acid is a yellow crystalline solid (m.p 395K) having a bitter taste whence it derives its name (Greek : *pikros* - bitter). The yellow colour is probably due to presence of quinonoid structure. It is somewhat insoluble in cold water but dissolves in hot water and in ether.

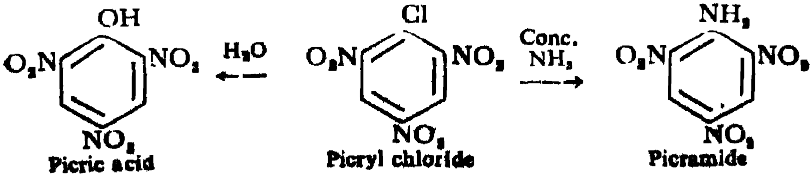
(*i*) Due to the presence of three negative —NO_2 groups it is stronger acid than phenol and decomposes carbonates.

(*ii*) Dry picric acid and its potassium or ammonium salt explodes violently when struck.

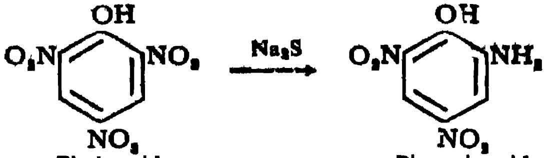
(*iii*) With bleaching powder picric acid gives chloropicrin as one of the products.

(*iv*) With aromatic hydrocarbons, amines and phenols, picric acid forms crystalline compounds called *picrates*

(*v*) With PCl_5 it forms *picryl chloride* in which the chlorine atom is very reactive on account of three nitro groups present in ortho and para positions. On boiling with water picryl chloride gives picric acid while on shaking with concentrated ammonia it gives *picramides*.



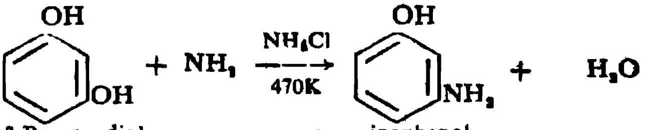
(*vi*) On reducing picric acid with sodium sulphide, we get *picramic acid.*



Picric acid   Picramic acid

Uses. It is used (*i*) in the manufacture of explosives; (*ii*) as a dye for wool and silk ; (*iii*) as an antiseptic in treatment of burns : and (*iv*) in the identification and isolation of aromatic hydrocarbons, amines and phenols.

7. **Aminophenols.**—These are prepared by reducing corresponding nitrophenols catalytically or with metal and acid. The *m*-isomer is prepared commercially by heating resorcinol with ammonia and ammonium chloride at 470K under pressure.



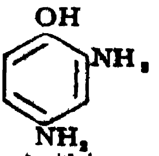
1, 3-Benzenediol   *m*-aminophenol

p-Aminophenol is prepared by electrolytic reduction of nitrobenzene in strong acid solution.

Properties and uses. *o*-, *m*- and *p*-Aminophenols are colourless solids (m.p. 410K, 396K and 459K respectively) which turn yellow or brown in air.

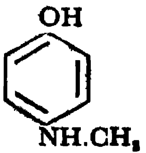
o- and *p*-Aminophenols are more weakly acidic than phenols and do not form phenoxides with alkalis but form salts with inorganic acids, *o*- and *p*-derivatives are readily oxidised to the corresponding quinones.

p-Aminophenol is used as a developer in photography. Two other important photographic developers are :



Amidol

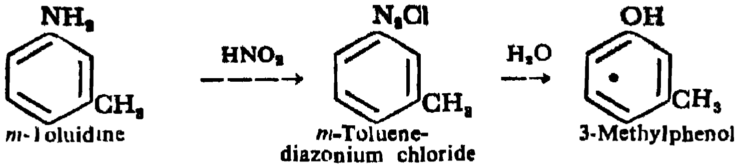
and

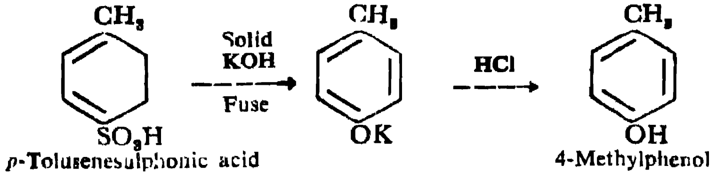


Metol

HOMOLOGUES OF PHENOL

8. **4-Methylphenol** *or* **4-Methylbenzenol**, $CH_3C_6H_4.OH$.—The methylphenols occur in the middle oil and heavy oil fractions of coal-tar. *o*-Isomer (b.p. 464K) is separated from the *m*- (b.p. 474K) and *p*-isomer (b.p. 498·5K) by fractional distillation using a good fractionating column. Each isomer could be obtained in its pure state from the corresponding toluidine or toluenesulphonic acid.





Properties. These are colourless substances having phenolic odour. Their properties have already been described under phenol.

The methyl group in methylphenols is not oxidised to a carboxyl group by chromic acid, nor is the ring attacked. In case –OH group is protected by acetylation or alkylation, the methyl group can be oxidised.

Uses. (*i*) Mixture of three methylphenols with a little phenol is called cresylic acid or creosote which finds use for preserving wood (timber, railway sleepers, etc.)

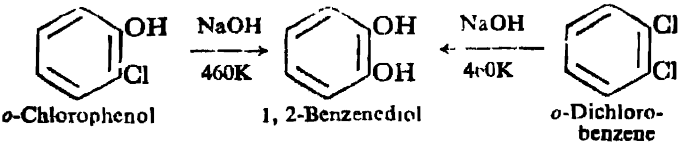
(*ii*) A soapy solution of methylphenols is known as *lysol*—a disinfectant.

(*iii*) methylphenols are used in the manufacture of resins, plasticisers, dyes and explosives.

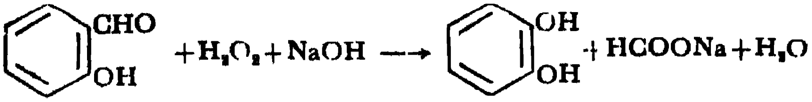
DIHYDRIC PHENOLS

9. **1, 2-Benzenediol** (*Common name* : *Catechol*).—It occurs in certain plants It was first obtained by the distillation of Indian *catechu* (product from *Acacia catechu* tree).

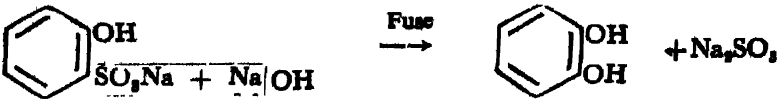
Preparation. (*i*) Commercially it is prepared by heating *o*-chlorophenol or *o*-dichlorobenzene with 20% NaOH solution and a trace of CuSO$_4$ at 460K under pressure.



(*ii*) It may be conveniently prepared in the laboratory *by treating salicylaldehyde with alkaline H_2O_2.*



or (*iii*) *By fusing o-hydroxybenzenesulphonic acid with sodium hydroxide.*



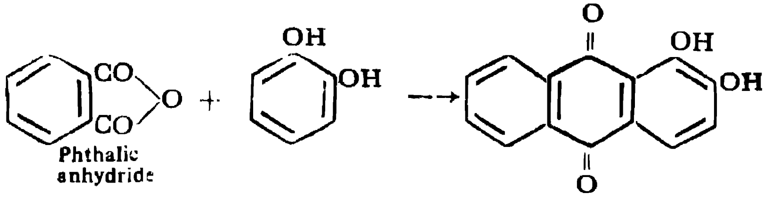
Properties. It is a colourless solid (m.p. 378K) soluble in water, alcohol and ether.

(1) With $FeCl_3$ it gives a green colour which changes red on adding Na_2CO_3.

(2) It is readily oxidised and, therefore, acts as a reducing agent. For example, (*i*) its aqueous solution darkens on exposure to air due to oxidation, (*ii*) it reduces $AgNO_3$ solution in cold and Fehling's solution on warming, and (*iii*) with silver oxide it is oxidised to *o*-benzoquinone.

(3) Its aqueous solution gives a white ppt. with lead acetate (distinction from *m*- and *o*-isomer).

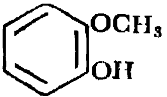
(4) 1, 2-Benzenediol condenses with a number of compounds, *e.g.*, it condenses with phthalic anhydride in the presence of sulphuric acid to form alizarin.



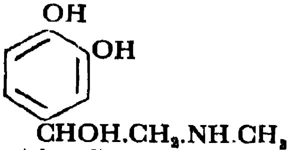
Phthalic anhydride

Alizarin

Two important derivatives of 1, 2-benzenediol are *guaiacol* and adrenaline (the hormone secreted by the adrenal glands).



Guaiacol



Adrenaline

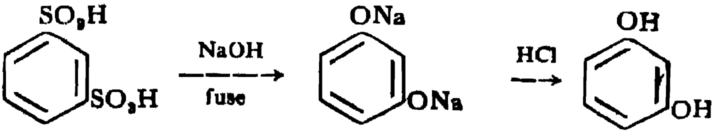
Uses. Catechol finds use : (*i*) As photographic developer.

(*ii*) In the manufacture of alizarin and adrenaline.

(*iii*) As an antioxidant in gasoline.

10. 1, 3-Benzenediol (*Common name : Recorcinol*).

Preparation. 1, 3-Benzenediol is prepared by *alkaline fusion of 1, 3-benzenedisulphonic acid* (*Industrial method*).

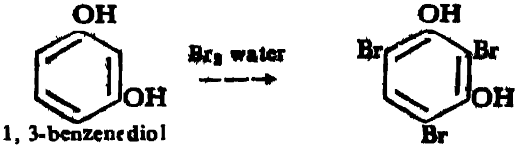


It is also obtained when *p*-disulphonic acid and many other *o*- and *p*-di-derivatives of benzene are treated in the same way, but how such remarkable change occurs, it is difficult to say.

Properties. It is a colourless crystalline solid (m.p., 383K) very soluble in water, alcohol and ether.

(*i*) In aqueous solution it gives a violet coloration with ferric chloride.

(*ii*) With bromine water it gives a precipitate of 2, 4, 6-tribromo-1, 3-benzenediol.

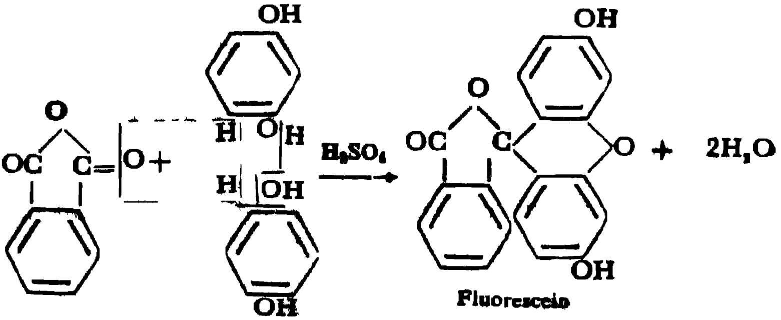


1, 3-benzenediol

2, 4, 6-tribromo-1, 3-benzenediol

(*iii*) It is not a powerful reducing agent like the *o*- and *p*-isomers but it reduces ammoniacal silver nitrate and Fehling's solution on warming.

(*iv*) It couples with diazonium salts to form azo-dyes. With phthalic anhydride it condenses to form fluorescein.

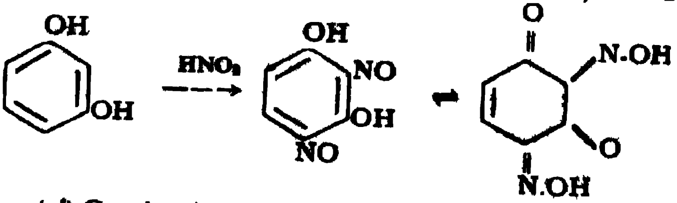


Phthalic anhydride

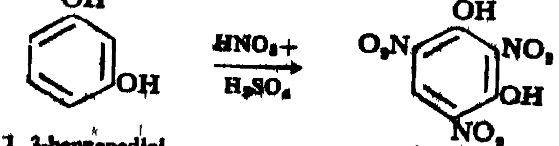
1, 3-benzenediol (*2 molecules*)

Fluorescein

(*v*) With nitrous acid it gives 2, 4-dinitroso-1, 3-benzenediol.



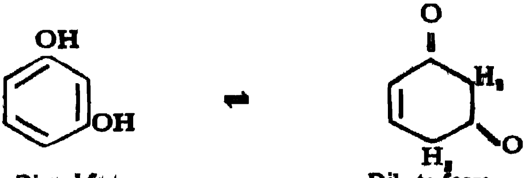
(*vi*) On nitration it forms styphnic acid (2, 4, 6-trinitro-1, 3-benzenediol.



1, 3-benzenediol

Styphnic acid

(vii) 1, 3-Benzenediol behaves as a tautomeric compound. This is shown by the fact that it forms a dioxime and a bisulphite compound.

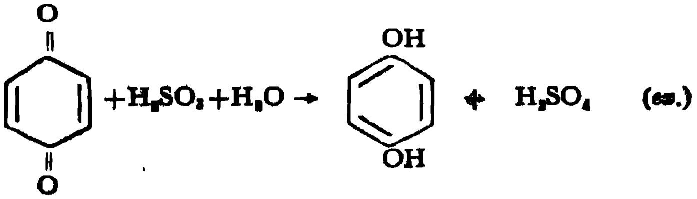


Dienol form Diketo form

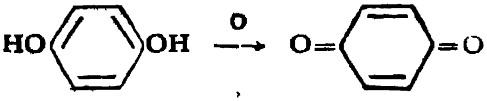
Uses. 1, 3-Benzenediol finds use : (*i*) For making dyes ; and (*ii*) As an antiseptic.

11. 1, 4-Benzenediol (*Common name* : *Quinol*).

Preparation. It is prepared by reducing *p*-benzoquinone with sulphurous acid.



Properties. It is a colourless, crystalline solid (m.p. 443K) very soluble in water, alcohol and ether, but insoluble in benzene. It gives a transient blue colour with $FeCl_3$ in water. It is a powerful reducing agent and finds use as a photographic developer. It is oxidised by ferric chloride to *p*-benzoquinone.



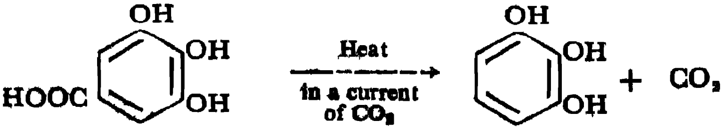
1, 4-Benzenediol *p*-Benzoquinone

Uses. (*i*) As a photographic developer ; and (*ii*) As an antiseptic.

TRIHYDRIC PHENOLS

12. 1, 2, 3-Benzenetriol (*Common name* : *Pyrogallol*).

Preparation. *1, 2, 3-Benzenetriol* is prepared by heating solid gallic acid in a current of CO_2 or by heating an aqueous solution of gallic acid at 480K under pressure.



Gallic acid (*solid*) 1, 2, 3-Benzenetriol

Properties. It is a colourless, crystalline solid (m.p. 485K) very soluble in water, alcohol and ether. An aqueous solution of 1, 2, 3-benzenetriol gives a red colour with $FeCl_3$. An alkaline solution of 1, 2, 3-benzenetriol rapidly oxidises on exposure to air and turns brown. It reduces the salts of silver, gold, platinum and mercury to their metals.

Uses. 1, 2, 3-Benzenetriol is used :

(*i*) As photographic developer ;

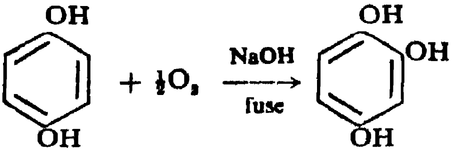
(*ii*) As hair dye ;

(*iii*) In antiseptic ointments ; and

(*iv*) In gas analysis for the absorption of oxygen and CO_2. During absorption 1, 2, 3-benzenetriol is oxidised to CO, CO_2, CH_3COOH, oxalic acid, etc.

13. 1, 2, 4-Benzenetriol (*Common name* : *Hydroxyquinol*).

Preparation. It is prepared by the alkaline fusion of 1, 4-benzenediol in air :



1, 4-benzenediol 1, 2, 4-benzenetriol

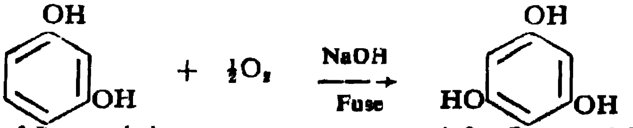
Properties. It is a colourless, crystalline solid (m.p 413K). It is very soluble in water and the aqueous solution gives greenish-brown colour with $FeCl_3$

14. 1, 3, 5-Benzenetriol (*Common name* : *Phloroglucinol*).

Preparation. It is obtained :

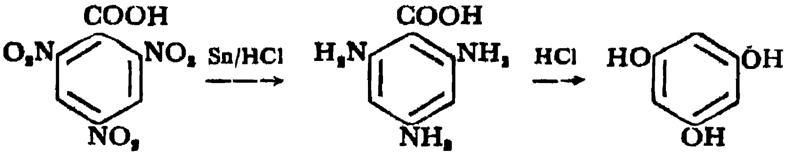
(*i*) When certain plant resins are fused with alkalis.

(*ii*) By fusing 1, 3-benzenediol with NaOH in air.



1, 3-Benzenediol 1, 3, 5-Benzenetriol

(*iii*) In the laboratory it can be conveniently prepared by reducing trinitrobenzoic acid and heating the amino-derivative obtained with hydrochloric acid.*



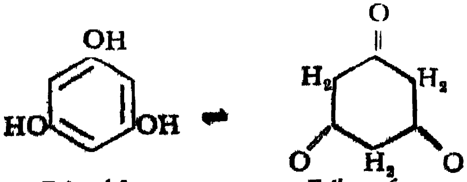
s-Trinitro-benzoic acid *s*-Triamino-benzoic acid 1, 3, 5-Benzenetriol $+CO_2+3NH_4Cl$

Properties and Uses. It is a colourless solid (m.p. 491K) fairly soluble in water. Its aqueous solution tastes sweet and gives a

---

*Decarboxylation and replacement of amino groups by hydroxyl groups on boiling *s*-Triaminobenzoic acid with hydrochloric acid is not a general reaction.

bluish violet colour with $FeCl_3$. Its alkaline solution darkens on standing in air due to oxidation. It is a tautomeric compound and exists in two forms.

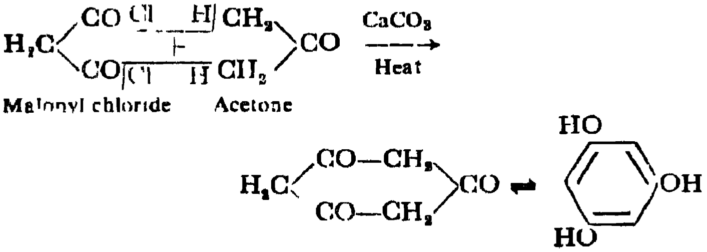


Trienol form *Triketo form*

Thus its trienol form gives a triacetate when warmed with acetic anhydride. It gives a tripotassium derivative and triethers.

The triketo form gives a trioxime when treated with hydroxylamine.

Existence of a tautomeric system was formerly supported by the statement that 1, 3, 5-Benzenetriol could be synthesised from acetone and malonyl chloride.



According to Elvidge (1932), however, no 1, 3, 5-Benzenetriol is obtained from malonyl chloride and acetone.

It gives red colour with carbohydrates in presence of sulphuric acid and is used in the detection of carbohydrates.

15. Phenolic Ethers.—Two important phenolic ethers are **methoxybenzene** (*Methyl phenyl ether, common name* : anisole) $C_6H_5.O.CH_3$ (b p. 428K) and **ethoxybenzene** (Ethyl phenyl ether, *common name* : phenetole), $C_6H_5.OC_2H_5$ (b.p. 445K). These are prepared :

(*i*) By heating sodium phenoxide with methyl or ethyl iodide or sulphate

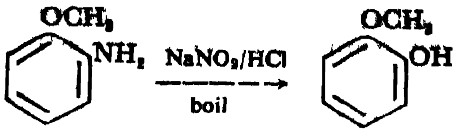
$$\underset{}{C_6H_5ONa+CH_3I \rightarrow \underset{\text{Methoxybenzene}}{C_6H_5OCH_3}+NaI} \qquad (v.g.)$$

$$C_6H_5ONa+(C_2H_5)_2SO_4 \rightarrow \underset{\text{Ethoxybenzene}}{C_6H_5OC_2H_5}+C_2H_5NaSO_4 \qquad (v.g.\text{-}ex.)$$

(*ii*) Methoxybenzene is easily obtained by the action of diazomethane on phenol.

$$C_6H_5OH+CH_2N_2 \rightarrow C_6H_5OCH_3+N_2 \qquad (ex.)$$

2-Methoxybenzenol or 2-Methoxyphenol (*common name* : Guaiacol) —m.p. 305K, b.p. 478K) is a benzenediol ether. It is prepared synthetically from *o*-anisidine.



It is used in medicine and in the preparation of vanillin.

AROMATIC ALCOHOLS

16. General—Aromatic alcohols are hydroxy compounds containing a hydroxyl group in the side-chain. These may be looked upon as aryl derivatives of aliphatic alcohols. These may be classified as primary, secondary and tertiary alcohols just like aliphatic alcohols and are prepared just like them. A few typical primary alcohols are discussed here.

17. Benzyl alcohol (Phenylmethanol), $C_6H_5CH_2OH$.—Benzyl alcohol occurs free and as ester in jasmine oil, Tolu and Peru balsams. It is a typical and simplest primary aromatic alcohol and is isomeric with methylbenzenol, $CH_3—C_6H_4—OH$.

Preparation. Benzyl alcohol may be prepared by methods analogous to those used for aliphatic primary alcohols, *e.g.*,

(*i*) *By reducing benzaldehyde with zinc and hydrochloric acid.*

$$\underset{\text{Benzaldehyde}}{C_6H_5-CHO}+2[H] \xrightarrow{\text{Zn/HCl}} \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH}$$

(*ii*) *By treating benzaldehyde with 50 per cent aqueous or alcoholic potash* (**Cannizzaro's reaction**).

$$\underset{\text{Benzaldehyde}}{2C_6H_5CHO}+KOH \longrightarrow \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH}+\underset{\text{Potassium benzoate}}{C_6H_5COOK}\ (90\%)$$

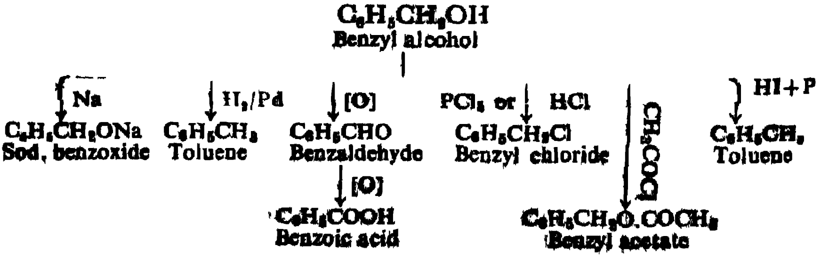
It may also be prepared by means of a crossed Cannizzaro reaction.

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO}+HCHO+NaOH \rightarrow \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH}+HCOONa$$

(*iii*) **Manufacture.** *By hydrolysing benzyl chloride with aqueous caustic soda.*

$$C_6H_5CH_2Cl+NaOH \longrightarrow C_6H_5CH_2OH+NaCl \quad (70\%)$$

Properties Benzyl alcohol is a colourless, pleasant-smelling liquid (b.p. 478K), sparingly soluble in water but readily soluble in organic solvents. It has anaesthetic properties. Its reactions are similar to those of primary aliphatic alcohols, *e.g.*



In addition to these reactions, benzyl alcohol exhibits the properties of the benzene nucleus, *e.g.*, it can be nitrated, sulphonated, etc., *o*- and *p*- derivative is obtained in each case.

While preparing nuclear-substituted derivatives of benzyl alcohol care must be taken to avoid reaction with the hydroxyl group. It is generally better to start with benzyl chloride, prepare the substitution product and then hydrolyse it to the alcohol.

Uses. Benzyl alcohol is used :

(*i*) As an antiseptic in ointments.

(*ii*) In the preparation of esters (acetate and benzoate) used in perfumery.

(*iii*) In the preparation of benzyl benzoate—a remedy for whooping cough and asthma.

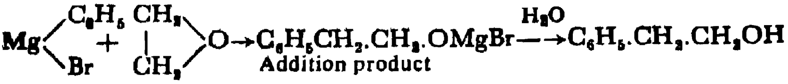
(*iv*) In the manufacture of synthetic resins.

18. β-Phenylethyl alcohol (*2-Phenylethanol*), **$C_6H_5CH_2.CH_2OH$**

It may be obtained by reducing phenylacetic ester with sodium and alcohol.

$$\underset{\text{Phenylacetic ester}}{C_6H_5CH_2COOC_2H_5} + 4[H] \rightarrow \underset{\text{2-Phenylethanol}}{C_6H_5CH_2CH_2OH} + C_2H_5OH$$

It is, however, manufactured by the action of ethylene oxide on phenylmagnesium bromide.



$$Mg\langle^{C_6H_5}_{Br} + \begin{matrix}CH_2\\|\\CH_2\end{matrix}\rangle O \rightarrow \underset{\text{Addition product}}{C_6H_5CH_2.CH_2.OMgBr} \xrightarrow{H_2O} C_6H_5.CH_2.CH_2OH$$

It is a colourless, sweet-smelling oily liquid (b.p. 295K) and is the chief constituent of rose oil. The alcohol and its esters are used in perfumery.

QUESTIONS

A. **Essay Type :**

1. What are phenols ? How do they differ from alcohols ? How can phenol be obtained from (*i*) benzene and (*ii*) aniline ? How can it be converted into (*i*) benzene ; (*ii*) aniline ; (*iii*) quinol ; (*iv*) phenolphthalein, salicylic acid, and cyclohexanol ?

What is the action of the following reagents on phenol : (*i*) Caustic soda ; (*ii*) Bromine ; (*iii*) Nitric acid ; (*iv*) Phosphorus pentachloride ; (*v*) Acetyl chloride ? (*Delhi B.Sc. 1977 ; B.Sc. Hons. Sub. 1976 ; Marathwada 1973*)

2. Describe two important methods for introducing an —OH group (phenolic group) in aromatic nucleus. Compare and contrast the properties of phenol with those of benzyl alcohol
(*Andhra B.Sc. 1975 ; Delhi B.Sc. Hons. Sub. 1977*)

3. Give three methods for preparation of phenol. Starting from phenol, how would you prepare chlorobenzene, benzene, aniline, methoxybenzene, cyclohexanol, picric acid ? (*Kerala B.Sc. 1973*)

4. How is phenol recovered from coal-tar ? How can it be converted to : (*i*) salicylic acid ; (*ii*) picric acid ; (*iii*) phenolphthalein ; (*iv*) *p*-hydroxyazobenzene ; (*v*) phenyl acetate ; and (*vi*) *p*-cresol.
(*Guru Nanak Dev B.Sc. 1971 ; Delhi 1980, 77*)

5. How many isomers are possible having the molecular formula C_7H_8O ? Name them. How can they be prepared and distinguished ?

6. Give the name and structural formula of each of three dihydric phenols. How can you prepare them? Describe their characteristic properties and uses. How is the hydroxyl group estimated?

7 What is 1, 3-benzenediol? How has it been synthetically prepared? Explain its use in the preparation of the organic dye 'fluorescein'.

8 (*a*) Write short notes on : (*i*) Benzenetriol, (*ii*) Benzyl alcohol

(*b*) How can you explain the fact that phenol is more easily attacked by electrophilic reagents than Nitrobenzene? (*Delhi B.Sc. 1972*)

9 How will you prepare the following :

(*i*) 3-methylphenol from *m*-toluenesulphonic acid. (*ii*) ethoxybenzene from phenol (*iii*) Phenyl acetate from benzene (*iv*) *m*-nitrophenol (*v*) *p*-nitrophenol (*vi* *p*-aminophenol (*vii*) *m* aminophenol. (*viii*) *m*-chlorophenol from benzene. (*ix*) *o*-Hydroxyacetophenone from phenol

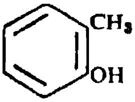
10. How will you separate

(*i*, Phenol, benzenesulphonic acid and benzyl alcohol.

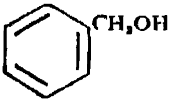
(*ii*) *o*- and *p*-Nitrophenol. (*iii*) Phenol and *p*-aminophenol

B. Short Answer Type :

1 How will you differentiate between



and



(*Delhi B Sc Hons 1977*)

2. How is phenol prepared from benzene and propene?
(*Guru Nanak Dev B Sc 1977*)

3 Generally, an unexpected question paper gives you headache. Phenol is a source of a headache relieving drug. What is its structural formula and how is it synthesised from phenol? (*Guru Nanak Dev B Sc 1977*)

4 What is the effect of chelation on the properties of *o*-nitrophenol?

5 Give one method of preparation of benzyl alcohol (*Kerala B Sc 1973*)

6 How will you convert phenol into (*i*) Salicyladehyde, (*ii*) cinnamic acid? (*Delhi B Sc 1976*)

7. Account for the following :

(*a*) Out of three isomeric nitrophenols only the *o*-isomer is steam volatile and its boiling point and solubility are lower as compared to the other isomers

(*b*) Unlike most phenols, 2, 4-dinitrophenol and 2, 4, 6-trinitrophenol are soluble in aqueous sodium bicarbonate

8 Formulate a reaction scheme to synthesise phenol from benzene and making use of Friedel-Crafts reaction (*Punjab B Sc. 1975*)

9 Give the probable mechanism of Reimer-Tiemann Reaction
(*Punjab B Sc 1976 Supp*)

10 Name the reagents and reaction conditions for the preparation of the following from phenol

(*i*) Salicylic acid (*ii*) *p*-Hydroxyacetophenone.
(*Punjab B.Sc. 1977*)

11. Arrange the following in the increasing order of acidity :

p-nitrophenol, *m*-aminophenol, *p*-methylphenol, 2,4-dinitrophenol. Give reasons for your answers. (*Punjab B Sc 1975*)

12 *o*-Nitrophenol is more acidic than *m*-nitrophenol. Why?
(*G.N.D. B.Sc. 1976*)

13. Boiling points of phenols are much higher than the boiling points of hydrocarbons of roughly the same molecular weight. Explain why.

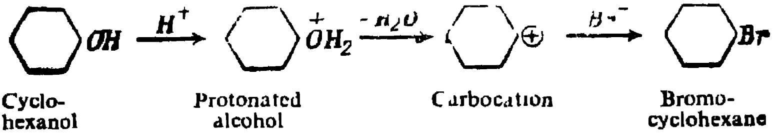
14. How do you account for appreciable water-solubilities of phenols ?

15 The carbon-oxygen bond of phenol is much stronger than that of an alcohol. For example cyclohexanol gives bromo-cyclohexane when refluxed with conc HBr whereas phenol does not react with conc HBr. Explain why.

Hint. In phenol carbon atom bearing OH group is sp^2 hybridised and that in cyclohexanol is sp^3 hybridised. C–O bond in phenol formed by sp^2-p overlap is shorter and stronger than the one in cyclohexanol formed by sp^3-p overlap.

Both phenol and phenoxide ion are stabilised by resonance, but phenoxide ion is stabilised to a greater extent than phenol It is, therefore, a strong acid and phenoxide ion being more stable C—O bond is very strong.

Cyclohexanol is a much weaker acid due to lack of resonance stabilisation and OH group is protonated and finally replaced by Br



16 Give electronic explanation for phenols being more acidic than alcohols (*Delhi B Sc 1980, Delhi B Sc Hons. 1980*)

17 Explain why *p*-nitrophenol is more acidic than phenol (*Delhi B Sc Hons Sub 1980*)

18. What reactions does phenol undergo with the following

(*i*) Acetic anhydride followed by $AlCl_3$ (anhydrous),

(*ii*) Nitric acid and sulphuric acid mixture,

(*iii*) Nitrous acid, (*iv*) Hexamethylene tetramine (urotropine),

(*v*) Distillation with zinc powder,

(*vi*) H_2/Ni catalyst ? (*Delhi B Sc 1979*)

19. Give reason why phenols couple more readily in slightly basic than in acidic solution. (*Osmania B.Sc 1980*)

20. What is Reimer-Tiemann reaction ? Give its mechanism (*Delhi B Sc Hons 1980*)

21. Rearrange the following as suggested giving brief explanations,

(*i*) In the order of increasing acidic strength picric acid, phenol, *o*-nitrophenol.

(*ii*) In order of increasing basic character aniline, ammonia, dimethylaniline (*Delhi B Sc. Hons 1980*)

C. Problems :

1. An organic compound C_8H_{10} (A) gives on disulphonation followed by fusion with alkali and acidification, two isomeric compounds B and C of the formula $C_8H_{10}O_2$. Oxidation of esters of B and C followed by hydrolysis gives two new isomeric compounds D and E of the formula $C_7H_6O_4$. Both D and E on decarboxylation yield $C_6H_6O_2$ (F) Identify various compounds from A to F.

2. The compound A is xylene. On sulphonation it gives only one product B which on alkaline fusion followed by acidification yields C, a phenol On treatment with chloroform and alkali C gives $C_9H_{10}O_2$ (D). Identify the various organic compounds from A to D.

3. An organic compound $C_6H_4O_2NCl$ (A) reacts with alkali to give $C_6H_5O_3N$ (B). On reduction with tin and HCl, B gives C_6H_7ON (C) whereas on milder reduction it gives $C_6H_7O_3N$(D) which rearranges in presence of a mineral acid to give a new compound E. Identify the various compounds from A to E.

4. An organic compound has the molecular formula $C_7H_8O_2$. It gives the following reactions :

(i) On oxidation with $KMnO_4$ *p*-hyroxybenzoic acid is formed.

(ii) When treated with PCl_5 a compound $C_7H_6Cl_2$ is obtained.

Assign structural formula to the compound and explain fully the reactions.

5. An organic liquid A is shaken with NaOH until the reaction is complete. The products of reaction are B and C. The composition of B is C$=$77·8% ; H$=$7·4% ; O$=$14·8% and its oxidation yields A. C is the sodium salt of an acid and gives on heating with soda-lime an aromatic hydrocarbon. Identify A, B and C.

6. The following reactions have been carried out :

$$\text{Nitrobenzene} \xrightarrow{Zn+NH_4Cl} \text{A } (C_6H_7ON), \textit{ N-phenyl-hydroxylamine}$$

$$\text{A} \xrightarrow{\text{acid}} \text{B } (C_6H_7ON)$$

$$\text{B} \xrightarrow{\text{reduction}} \text{Aniline}$$

$$\text{B} \xrightarrow{\text{oxidation}} \text{Nitrosobenzene}$$

$$\text{B} \xrightarrow{\text{Acetic anhydride}} \text{C } (C_8H_9O_2N) \xrightarrow{\text{Acetic anhydride}} \text{D } (C_{10}H_{11}O_3N)$$

$$\text{C} \xrightarrow{(CH_3)_2SO_4,\ OH^-} \text{E } (C_9H_{11}O_2N) \xrightarrow{OH^-,\ \text{heat}} \text{F } (C_7H_9ON)$$

$$\text{F} \xrightarrow{NaNO_2,\ H_2SO_4} \quad \xrightarrow{\text{CuBr}} p\text{-Bromomethoxybenzene}$$

Solubility behaviour of various compounds :

	dil HCl	*dil NaOH*	*aq $NaHCO_3$*
B	sol.	sol.	insol.
C	insol.	sol.	insol.
D	insol.	insol.	insol.
E	insol.	insol.	insol.
F	sol.	insol.	insol.

(a) What are the structures of compounds B to F.

(b) What would you get instead of B if you started with *m*-nitrotoluene ?

(c) Outline a possible synthesis of 3-methyl-4-aminophenol starting from toluene.

ANSWERS

A. 9. *(i)* Alkali fusion followed by treatment with HCl.

(ii) $$C_6H_5OH \xrightarrow[+NaOH]{C_2H_5I} C_6H_5OC_2H_5.$$

(iii) $$C_6H_6 \xrightarrow{H_2SO_4} C_6H_5SO_3H \xrightarrow[\text{fusion}]{\text{Alkali}} C_6H_5OH \xrightarrow[+CH_3COONa]{(CH_3CO)_2O} C_6H_5O.OC.CH_3$$

(iv) Reduction of *m*-dinitrobenzene with $(NH_4)_2S$ followed by diazotization and heating

(v) Nitration of phenol with dil. HNO_3 followed by steam-distillation to remove the volatile *o*-isomer.

(vi) Reduction of *p*-nitrophenol obtained in *(v)* above ; or reduction of nitrobenzene with Zn dust and NH_4Cl to C_6H_5NOH followed by rearrangement in presence of conc. mineral acid.

(*vii*) Reduction of *m*-nitrophenol obtained in (*iv*) above.

(*viii*) $C_6H_6 \xrightarrow{H_2SO_4} C_6H_5SO_3H \xrightarrow{Cl_2} m\text{-}ClC_6H_4SO_3H \xrightarrow[\text{fusion}]{\text{Alkali}} m\text{-}ClC_6H_4OH$

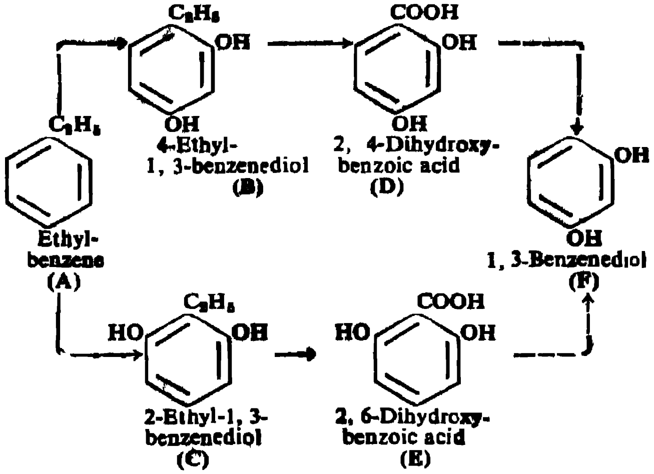
(*ix*) $C_6H_5OH \xrightarrow{\text{as in }(ii)} C_6H_5O.OCCH_3 \xrightarrow{AlCl_3}$ *o*- and *p*-hydroxyacetophenone. The *o*-isomer is steam volatile and can be removed.

10. **Hints :** (*i*) Add $NaHCO_3$ and extract C_6H_5OH and $C_6H_5CH_2OH$ with ether. From this extract C_6H_5OH with NaOH.

(*ii*) *o*-isomer is steam-volatile.

(*iii*) Add HCl and extract phenol with ether.

C. 1.



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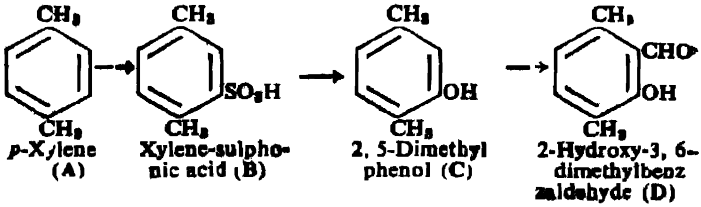

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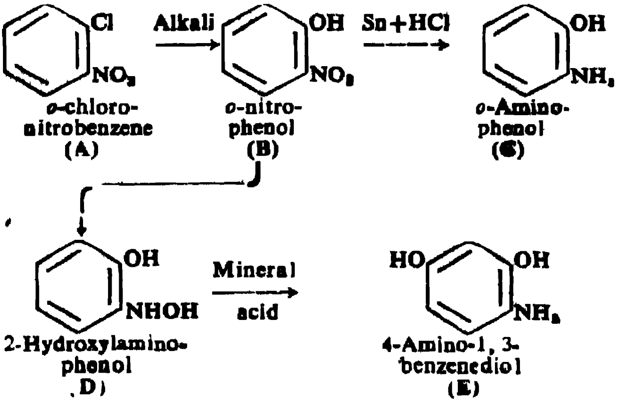

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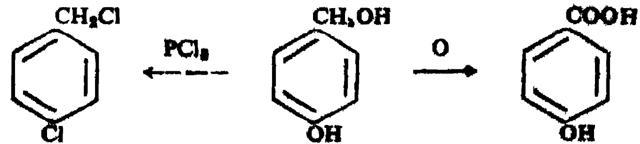


p-Chloro-benzyl chloride ← *p*-Hydroxy-benzyl alcohol → *p*-Hydroxy-benzoic acid

5. Mol. formula of B is C_7H_8O and possible isomers are:

$C_6H_5CH_2OH$; Benzyl alcohol

$C_6H_5—OCH_3$ Methoxybenzene

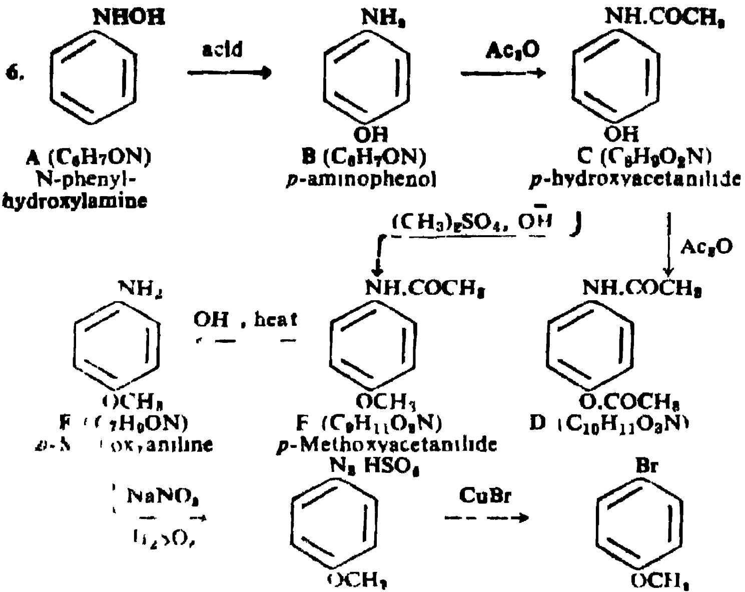
$C_6H_4{<}\begin{smallmatrix}CH_3\\OH\end{smallmatrix}$

o-, *m*-, or *p*-methylphenol

$$\underset{\substack{\text{Benzaldehyde}\\(A)}}{2C_6H_5CHO} + NaOH \rightarrow \underset{\substack{\text{Benzyl alcohol}\\(B)}}{C_6H_5CH_2OH} + \underset{\substack{\text{Sod. benzoate}\\(C)}}{C_6H_5COONa}$$

$$\underset{\substack{\text{Sod. benzoate}\\(C)}}{C_6H_5\overline{|COONa} + \underset{\text{Soda-lime}}{\overline{NaOH}|}} \rightarrow \underset{\substack{\text{Benzene}\\(\textit{aromatic hydrocarbon})}}{C_6H_6} + Na_2CO_3$$

6.



A (C_6H_7ON) N-phenyl-hydroxylamine

B (C_6H_7ON) *p*-aminophenol

C ($C_8H_9O_2N$) *p*-hydroxyacetanilide

D ($C_{10}H_{11}O_3N$)

F ($C_9H_{11}O_2N$) *p*-Methoxyacetanilide

F (C_7H_9ON) *p*-Methoxyaniline

o-bromo -methoxybenzene

43

Aromatic Aldehydes and Ketones

1. The Aromatic Aldehydes.—There are two types of aromatic aldehydes :

(*i*) *Those in which the aldehyde group, —CHO is directly attached to the benzene nucleus, e.g.,* benzaldehyde, C_6H_5CHO. Though resembling aliphatic aldehydes to some extent, these differ from them in some important respects.

(*ii*) *Those with aldehyde group present in the side chain, e.g.,* phenylacetaldehyde, $C_6H_5CH_2CHO$. They closely resemble aliphatic aldehydes.

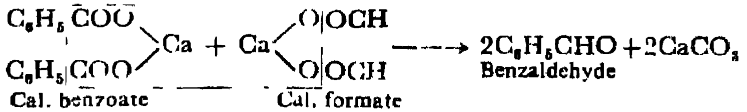
2. Benzaldehyde (Benzenecarbaldehyde), C_6H_5CHO.—Benzaldehyde is the simplest and the most important member of the aromatic aldehydes. It occurs as glucoside, *amygdalin* in bitter almonds and is, therefore, commonly known as *oil of bitter almonds.*

Amygdalin on hydrolysis with dilute acids or the enzyme emulsin gives benzaldehyde, glucose and hydrogen cyanide.

$$\underset{\text{Amygdalin}}{C_{20}H_{27}O_{11}N}+2H_2O \longrightarrow \underset{\text{Benzaldehyde}}{C_6H_5CHO}+\underset{\text{Glucose}}{2C_6H_{12}O_6}+HCN$$

Preparation. Benzaldehyde may be prepared by any of the following methods which are general for the homologues as well.

(1) *By the dry distillation of calcium benzoate with calcium formate*



$$\underset{\text{Cal. benzoate}}{\begin{matrix}C_6H_5COO\\C_6H_5COO\end{matrix}}\!\!>\!Ca+Ca\!<\!\!\underset{\text{Cal. formate}}{\begin{matrix}OOCH\\OOCH\end{matrix}}\longrightarrow \underset{\text{Benzaldehyde}}{2C_6H_5CHO}+2CaCO_3$$

(2) *By the catalytic reduction of benzoyl chloride.* Hydrogen is bubbled through benzoyl chloride in xylene solution in the presence of palladium catalyst until the calculated quantity of hydrogen chloride has been evolved (**Rosenmund's reaction**). The liquid is then acidified and steam-distilled. To prevent further reduction of benzaldehyde a quinoline-sulphur poison is added.

$$\underset{\text{Benzoyl chloride}}{C_6H_5COCl}+H_2\xrightarrow{Pd}\underset{\text{Benzaldehyde}}{C_6H_5CHO}+HCl \qquad (v.g)$$

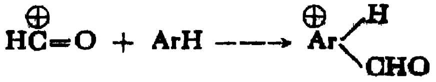
Benzoyl chloride can also be reduced to benzaldehyde by treating it with lithium tri *tert*-butoxyaluminium hydride,

$$LiAlH\ [OC(CH_3)_3]_3$$

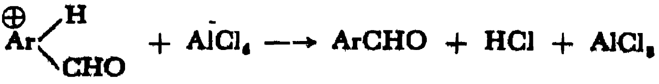
(3) *By passing a mixture of carbon monoxide and hydrogen chloride under high pressure (90 atm) through benzene in presence of anhydrous aluminium chloride and a small amount of cuprous chloride* (**Gattermann-Koch aldehyde synthesis**). Although formyl chloride (HCOCl) and formic anhydride $(HCO)_2O$ are unknown compounds,

the ion $HC{\equiv}O^+$, needed for **formylation** can be produced by protonation of carbon monoxide in presence of HCl and $AlCl_3$.

$$:C{=}O + HCl + AlCl_3 \rightleftharpoons \left[H\overset{\oplus}{C}{=}O \longleftrightarrow HC{\equiv}\overset{\oplus}{O}\right] AlCl_4^-$$



$$H\overset{\oplus}{C}{=}O + ArH \longrightarrow \overset{\oplus}{Ar}\begin{matrix}\diagup H \\ \diagdown CHO\end{matrix}$$



$$\overset{\oplus}{Ar}\begin{matrix}\diagup H \\ \diagdown CHO\end{matrix} + \overset{-}{AlCl_4} \longrightarrow ArCHO + HCl + AlCl_3$$

Protonation of HCN produces a similar electrophile. Solid zinc cyanide is often used as an *in situ* source of HCN.

$$HC{\equiv}N + HCl + AlCl_3 \longrightarrow H\overset{\oplus}{C}{=}NH + AlCl_4^-$$

$$H\overset{\oplus}{C}{=}NH + Ar\,H \longrightarrow ArCH{=}\overset{+}{N}H_2$$

$$ArCH{=}\overset{+}{N}H_2 + H_2O + Al\overset{-}{Cl}_4 \rightarrow ArCHO + NH_3 + AlCl_3 + HCl$$

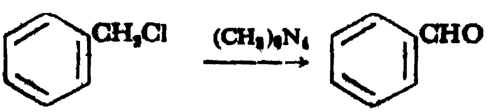
Even though they are virtually the same reaction, the aldehyde synthesis with HCN is called **Gattermann synthesis**.

(4) **Stephen's Method** (1925). *By reduction of phenyl cyanide with stannous chloride and hydrogen chloride in ethereal solution on hydrolysing the product with water.*

$$\underset{\text{Phenyl cyanide}}{C_6H_5C{\equiv}N} \xrightarrow{SnCl_2/HCl} \underset{\text{Imino chlorostannate}}{[C_6H_5CH{=}\overset{+}{N}H_2]\,[H\overset{-}{S}nCl_6]}$$

$$\xrightarrow{H_2O} \underset{\text{Benzaldehyde}}{C_6H_5CH{=}O} \qquad (v\,g)$$

(5) **Sommelet Reaction**. *By refluxing benzyl chloride with hexamethylenetetramine in aqueous alcoholic solution followed by acidification and steam-distillation.*

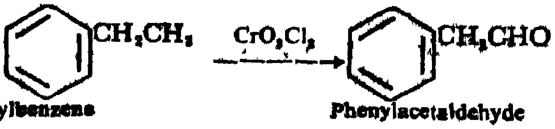


(60-70%)

(6) **Etard Reaction**. *By treating toluene with chromyl chloride in carbon tetrachloride and decomposing the complex precipitated with water.*

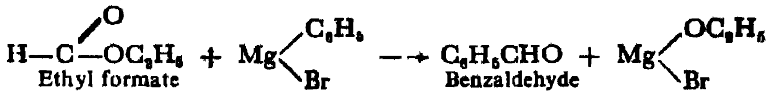
$$\underset{\text{Toluene}}{C_6H_5CH_3} \xrightarrow[CCl_4]{CrO_2Cl_2} \underset{\text{Complex pptd.}}{C_6H_5CH(OCrOHCl_2)_2} \xrightarrow{H_2O} \underset{\text{Benzaldehyde}}{C_6H_5CHO}\ (90\%)$$

Side-chains bigger than CH_3 are oxidised by CrO_2Cl_2 at the end carbon atom, *e.g.*,



Ethylbenzene Phenylacetaldehyde

(7) **Grignard Reaction.** *By treating phenylmagnesium bromide with ethyl formate.*



$$\underset{\text{Ethyl formate}}{H-\overset{O}{\overset{\|}{C}}-OC_2H_5} + Mg\begin{cases}C_6H_5\\ Br\end{cases} \longrightarrow \underset{\text{Benzaldehyde}}{C_6H_5CHO} + Mg\begin{cases}OC_2H_5\\ Br\end{cases}$$

(8) **From Diazonium Salt.** By treating diazonium salt with formaldoxime ($CH_2=NOH$).

$$C_6H_5N_2Cl \xrightarrow{CH_2=NOH} \underset{\text{Benzaldoxime}}{C_6H_5CH=NOH} \xrightarrow{H_2O} \underset{\text{Benzaldehyde}}{C_6H_5CHO} \ (40\%)$$

(9) **Laboratory Methods.** (*i*) By boiling benzyl chloride with aqueous solution of copper or lead nitrate in a current of carbon dioxide The mechanism of the reaction is not known.

$$2C_6H_5\,CH_2Cl + Pb(NO_3)_2 \rightarrow 2C_6H_5.CHO + PbCl_2 + 2HNO_2 \ (40\%)$$

Expt. A mixture of benzyl chloride (10 g), copper nitrate (8 g) and water (50 ml) is refluxed in a current of CO_2 for about six hours. The contents are cooled and benzaldehyde is extracted with ether and treated with sodium bisulphite. The bisulphite crystals are decomposed with dilute sulphuric acid and the benzaldehyde extracted with ether and distilled.

This method has also been used to prepare benzaldehyde commercially.

(*ii*) It may also be conveniently prepared in the laboratory by oxidation of toluene with chromic anhydride in acetic anhydride. Benzaldehyde formed gives benzylidene acetate and thus prevents further oxidation of benzaldehyde Benzylidene acetate on hydrolysis with dilute acid gives benzaldehyde.

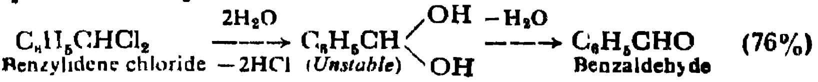
$$\underset{\text{Toluene}}{C_6H_5CH_3} \xrightarrow[(CH_3CO)_2O]{CrO_3+} \underset{\text{Benzylidene acetate}}{C_6H_5CH(OOCCH_3)_2} \xrightarrow{H_2O}$$

$$C_6H_5CHO + 2CH_3COOH \qquad (40\text{-}50\%)$$

(*iii*) A much better yield (about 90%) of benzaldehyde is obtained by oxidation of benzyl alcohol with chromic anhydride in acetic anhydride or with acidified dichromate.

$$\underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} \xrightarrow{O} \underset{\text{Benzaldehyde}}{C_6H_5CHO}$$

(10) **Manufacture.** (*a*) *By heating benzylidene chloride (obtained by chlorination of toluene) with water at 370K, in the presence of iron powder as catalyst.*



$$\underset{\text{Benzylidene chloride}}{C_6H_5CHCl_2} \xrightarrow[-2HCl]{2H_2O} \underset{(\textit{Unstable})}{C_6H_5CH\begin{cases}OH\\ OH\end{cases}} \xrightarrow{-H_2O} \underset{\text{Benzaldehyde}}{C_6H_5CHO} \quad (76\%)$$

(*b*) *By partial oxidation of toluene with manganese dioxide and 65 per cent sulphuric acid at 310K (liquid phase oxidation).*

$$\underset{\text{Toluene}}{C_6H_5CH_3} + 2[O] \xrightarrow{MnO_2+H_2SO_4} \underset{\text{Benzaldehyde}}{C_6H_5CHO} + H_2O$$

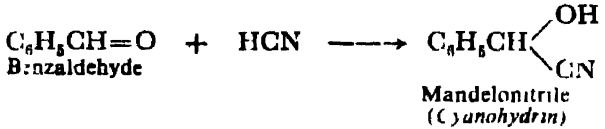
Toluene may also be catalytically oxidised with air diluted with nitrogen at 770K in presence of oxides of manganese, molybdenum or zirconium (*vapour phase oxidation*).

Properties : Physical. Benzaldehyde is a colourless highly refractive liquid (b.p. 443K ; refractive index 1·55) slightly heavier than water (density 1·05) having characteristic smell of bitter almonds. It is only slightly soluble in water but readily soluble in alcohol and ether. It is volatile in steam and poisonous in nature.

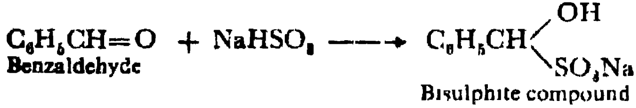
Chemical. The molecule of benzaldehyde consists of the benzene nucleus and an aldehyde group. Benzaldehyde (and aromatic aldehydes in general) differs from aliphatic aldehydes in certain respects because of the aldehyde group being linked to the phenyl group. Most of its reactions, however, are typical of the aliphatic aldehydes as given below :

(*a*) **Common Reactions of Benzaldehyde and aliphatic aldehydes :**

(1) **Addition Reactions.** Benzaldehyde forms a cyanohydrin with hydrogen cyanide and a bisulphite compound with sodium bisulphite. It is generally obtained pure *via* the bisulphite compound



$$\underset{\text{Benzaldehyde}}{C_6H_5CH{=}O} + HCN \longrightarrow \underset{\substack{\text{Mandelonitrile}\\ (\textit{Cyanohydrin})}}{C_6H_5CH\begin{array}{l}\diagup OH\\ \diagdown CN\end{array}}$$

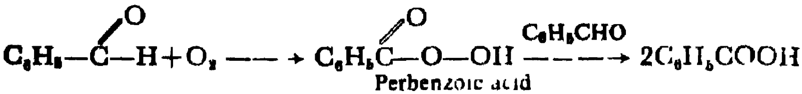


$$\underset{\text{Benzaldehyde}}{C_6H_5CH{=}O} + NaHSO_3 \longrightarrow \underset{\text{Bisulphite compound}}{C_6H_5CH\begin{array}{l}\diagup OH\\ \diagdown SO_3Na\end{array}}$$

(2) **Oxidation.** Benzaldehyde is oxidised to benzoic acid even on exposure to air

$$\underset{\text{Benzaldehyde}}{2C_6H_5CHO} + O_2 \longrightarrow \underset{\text{Benzoic acid}}{2C_6H_5COOH}$$

Baeyer and Villiger (1900) suggested that this oxidation occurs *via* the formation of perbenzoic acid.



$$C_6H_5-\overset{\displaystyle O}{\overset{\|}{C}}-H+O_2 \longrightarrow \underset{\text{Perbenzoic acid}}{C_6H_5\overset{\displaystyle O}{\overset{\|}{C}}-O-OH} \xrightarrow{C_6H_5CHO} 2C_6H_5COOH$$

At present, however, it is believed that oxidation proceeds *via* free peroxide radical.

(3) **Reduction.** Benzaldehyde on reduction with zinc and hydrochloric acid or with sodium amalgam and water gives hydrobenzoin, and benzyl alcohol (*cf.*, acetaldehyde which gives ethyl alcohol).

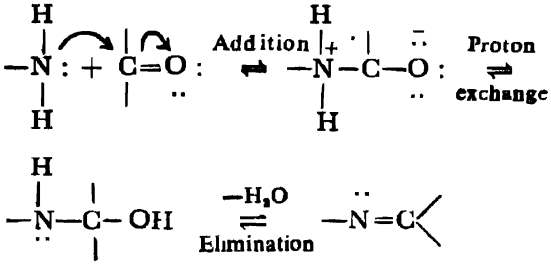
$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + 2[H] \longrightarrow \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH}$$

$$2C_6H_5CHO + 2[H] \longrightarrow \underset{\text{Hydrobenzoin}}{C_6H_5.CHOH.CHOH.C_6H_5}$$

(4) **Reducing Properties.** Benzaldehyde is readily oxidised and thus acts as a strong reducing agent, *e.g.*, it reduces ammoniacal silver nitrate to silver mirror, itself being oxidised to benzoic acid.

$$C_6H_5CHO+2Ag(NH_3)_2^{+}+3OH^{-} \longrightarrow 2Ag+C_6H_5COO^{-} + 4NH_3$$

(5) **Addition-Elimination Reactions.** Aldehydes and ketones react with a number of derivatives of ammonia in the general way involving addition to $>C{=}O$ group followed by elimination of a molecule of water as shown below :



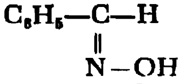
Some specific examples are :

(i) Benzaldehyde reacts *with hydroxylamine and phenylhydrazine* to give an oxime and phenylhydrazone respectively.

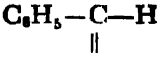
$$C_6H_5CH{=}O + \underset{\text{Hydroxylamine}}{H_2\,NOH} \longrightarrow \underset{\text{Benzaldoxime}}{C_6H_5CH{=}NOH} + H_2O$$

$$C_6H_5CH{=}O + H_2N.NHC_6H_5 \longrightarrow \underset{\text{Phenylhydrazone}}{C_6H_5CH{=}N.NHC_6H_5} + H_2O$$

Benzaldoxime exists in two geometrical isomeric forms.



Syn-form



Anti-form

(ii) *With hydrazine* it forms benzylideneazine.

$$2C_6H_5CH{=}O + H_2N.NH_2 \longrightarrow \underset{\text{Benzylideneazine}}{C_6H_5CH{=}N{-}N{=}CH.C_6H_5} + 2H_2O$$

(6) **Replacement of Carbonyl Oxygen.** Benzaldehyde reacts with phosphorus pentachloride when the carbonyl oxygen is replaced by two chlorine atoms to form benzylidene chloride.

$$C_6H_5CHO + PCl_5 \longrightarrow \underset{\text{Benzylidene chloride}}{C_6H_5CHCl_2} + POCl_3$$

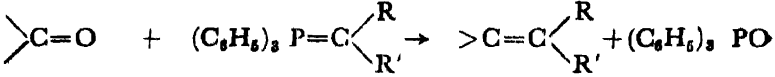
(7) **Tischenko Reaction.** On heating benzaldehyde with aluminium alkoxide (ethoxide or isopropoxide) and a little anhydrous $AlCl_3$ or $ZnCl_2$, it undergoes an intermolecular oxidation and reduction similar to Cannizzaro reaction but the alcohol and acid instead of appearing as such, react to produce benzyl benzoate.

$$\underset{\text{Benzaldehyde}}{2C_6H_5CHO} \xrightarrow{Al(OC_2H_5)_3} \underset{\text{Benzyl benzoate}}{C_6H_5CH_2OOCC_6H_5}$$

(*cf.*, CH_3CHO which gives $CH_3.CH_2.OOCCH_3$)

(8) **Schiff's Reaction.** It gives a pink colour with Schiff's reagent (rosaniline hydrochloride solution in water decolorised by passing sulphur dioxide). The mechanism of the reaction is obscure

(9) **Wittig Reaction.** Aldehydes and ketones react with phosphorus ylides *e.g.*, alkylidene triphenylphosphoranes [$(C_6H_5)_3$ P=CRR′ where R and R′ may be alkyl or aryl groups or hydrogen atoms].



$$>C=O + (C_6H_5)_3P=C\langle^{R}_{R'} \rightarrow >C=C\langle^{R}_{R'} + (C_6H_5)_3PO$$

An aldehyde or ketone — An ylide — Substituted alkene — Triphenyl phosphine oxide

$C_6H_5CH=O + (C_6H_5)_3P=CH_2 \rightarrow C_6H_5CH=CH_2 + (C_6H_5)_3PO$

Benzaldelyde — Methylene triphenyl phosphorane — Styrene

(*b*) **Reactions of Benzaldehyde different from aliphatic aldehydes :**

(1) **With Fehling's solution.** Unlike aliphatic aldehydes, benzaldehyde does not reduce Fehling's solution.

(2) **With ammonia.** It does not yield a simple addition product with ammonia but gives a complex product *hydrobenzamide*, $(C_6H_5CH)_3N_2$ or $C_6H_5CH(—N=CH.C_6H_5)_2$ (*cf.*, acetaldehyde which gives aldehyde ammonia and formaldehyde which gives hexamethylenetetramine).

$3C_6H_5CHO + 2NH_3 \longrightarrow (C_6H_5CH)_3N_2 + 3H_2O$ (90%)

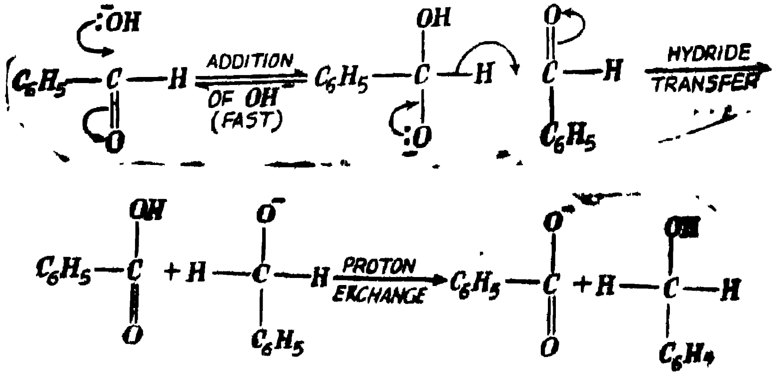
Benzaldehyde — Hydrobenzamide — evei

(3) **With caustic soda.** Benzaldehyde does not give any resinous mass with sodium hydroxide (*cf.*, acetaldehyde) but undergoes **Cannizzaro reaction** (*cf.*, formaldehyde). Two molecules of benzaldehyde take part in the reaction, one is reduced to benzyl alcohol while the other is oxidised to benzoic acid.

$2C_6H_5CHO + NaOH \longrightarrow C_6H_5CH_2OH + C_6H_5COONa$

Benzaldehyde — Caustic soda — Benzyl alcohol — Sodium benzoate

The mechanism involves hydride ion transfer, one possibility being as follows :

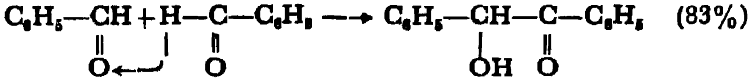


As formaldehyde is oxidised more readily than benzaldehyde, the latter is completely converted to benzyl alcohol when a mixture of benzaldehyde with excess of formaldehyde is heated with concentrated aqueous sodium hydroxide (**crossed Cannizzaro reaction**).

$$C_6H_5CHO + HCHO + NaOH \longrightarrow C_6H_5CH_2OH + HCOONa$$

Benzaldehyde Benzyl alcohol

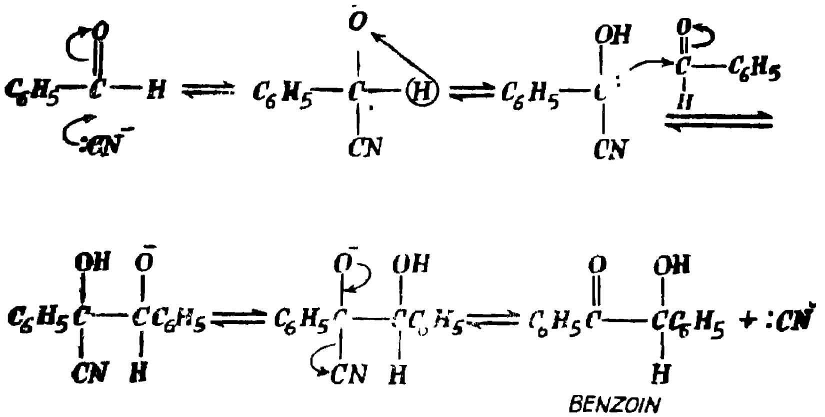
(4) **Benzoin Condensation.** Benzoin is formed by condensation of benzaldehyde when refluxed with aqueous alcoholic potassium cyanide solution.



$$\underset{O}{\overset{\|}{C_6H_5-CH}} + \underset{O}{\overset{\|}{H-C}}-C_6H_5 \longrightarrow C_6H_5-\underset{OH}{\overset{|}{CH}}-\underset{O}{\overset{\|}{C}}-C_6H_5 \quad (83\%)$$

Benzaldehyde (*Two molecules*) Benzoin

Mechanism of the Reaction. The generally accepted mechanism of benzoin condensation is as follows :



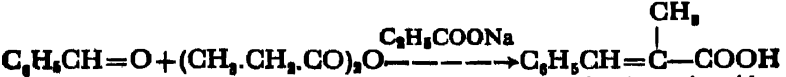
(5) **Other Condensation Reactions.** It condenses with certain compounds (aliphatic and aromatic) with the elimination of a molecule of water yielding an unsaturated product in each case.

(*a*) **Perkin's Reaction** (1877). Benzaldehyde (or any other aromatic aldehyde) when heated with the anhydrous sodium salt of a fatty acid (containing two α-hydrogen atoms) and its anhydride, gives an unsaturated acid. For example, with acetic anhydride and sodium acetates, benzaldehyde gives cinnamic acid.

$$C_6H_5CHO + (CH_3CO)_2O \xrightarrow{CH_3COONa} C_6H_5CH{=}CHCOOH + CH_3COOH$$

Benzaldehyde Acetic anhydride Cinnamic acid

With propionic anhydride and sodium propionate, it gives α-methylcinnamic acid.

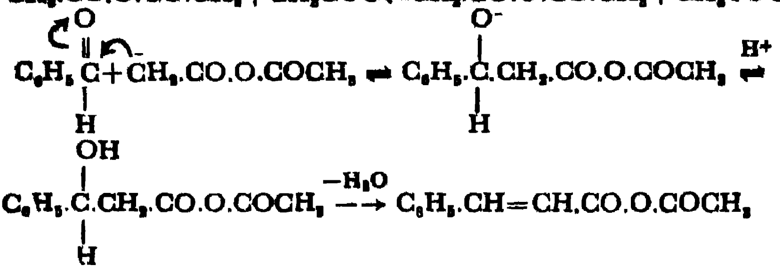


$$C_6H_5CH{=}O + (CH_3.CH_2.CO)_2O \xrightarrow{C_2H_5COONa} C_6H_5CH{=}\overset{\overset{CH_3}{|}}{C}-COOH$$

α-methylcinnamic acid

Mechanism of the reaction. The reaction is believed to take place as follows through the formation of a carbanion.

$CH_3.CO.O.CO.CH_3 + CH_3CO\bar{O} \rightleftharpoons \bar{C}H_2.CO.O.CO.CH_3 + CH_3COOH$



$$C_6H_5\overset{O}{\underset{H}{C}} + \bar{C}H_2.CO.O.COCH_3 \rightleftharpoons C_6H_5.\overset{O^-}{\underset{H}{C}}.CH_2.CO.O.COCH_3 \xrightleftharpoons{H^+}$$

$$C_6H_5.\overset{OH}{\underset{H}{C}}.CH_2.CO.O.COCH_3 \xrightarrow{-H_2O} C_6H_5.CH=CH.CO.O.COCH_3$$

$$\xrightarrow{H_2O} \underset{\text{Cinnamic acid}}{C_6H_5CH=CH.COOH} + CH_3COOH$$

(*b*) **Knoevenagel Reaction.** With malonic acid in ethanolic ammonia in presence of pyridine benzaldehyde undergoes Knoevenagel reaction to give cinnamic acid.

$$C_6H_5CH=O + \underset{\text{Malonic acid}}{CH_2(COOH)_2} \xrightarrow{\text{Pyridine}} \underset{\text{Cinnamic acid}}{C_6H_5CH=CH.COOH} + CO_2 + H_2O$$

(*c*) **Claisen-Schmidt Reaction (also known as the Claisen reaction).** Benzaldehyde, in the presence of dilute alkali, condenses with aliphatic aldehydes or ketones containing α-hydrogen, *e.g.*, with acetaldehyde it gives cinnamaldehyde.

$$\underset{\text{Benzaldehyde}}{C_6H_5CH=}\boxed{O+H_2}\underset{\text{Acetaldehyde}}{CH.CHO} \xrightarrow{NaOH} \underset{\text{Cinnamaldehyde}}{C_6H_5CH=CH.CHO} + H_2O$$

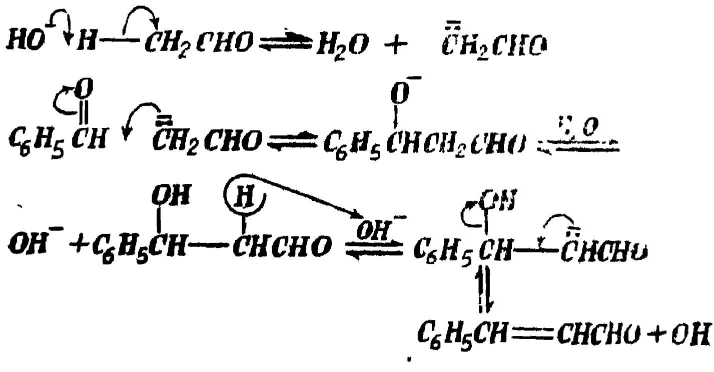
With acetone it gives benzylidene-acetone (used in perfumery)

$$C_6H_5CH=\boxed{O+H_2}CH.COCH_3 \longrightarrow \underset{\text{Benzylideneacetone}}{C_6H_5CH=CH.COCH_3}$$

In presence of aqueous alcoholic sodium hydroxide dibenzylideneacetone is produced.

$$2C_6H_5CH=O + CH_3.CO.CH_3 \rightarrow \underset{\text{Dibenzylideneacetone}}{(C_6H_5-CH=CH)_2CO} + 2H_2O$$

The mechanism of the Claisen-Schmidt reaction is as follows :



$$HO^- + H-CH_2CHO \rightleftharpoons H_2O + \bar{C}H_2CHO$$

$$C_6H_5\overset{O}{\overset{\|}{CH}} + \bar{C}H_2CHO \rightleftharpoons C_6H_5\overset{O^-}{\overset{|}{CH}}CH_2CHO \xrightleftharpoons{H_2O}$$

$$OH^- + C_6H_5\overset{OH}{\overset{|}{CH}}-\overset{H}{\overset{|}{CH}}CHO \xrightleftharpoons{OH^-} C_6H_5\overset{OH}{\overset{|}{CH}}-\bar{C}HCHO$$

$$\Downarrow$$

$$C_6H_5CH=CHCHO + OH^-$$

Cinnamaldehyde

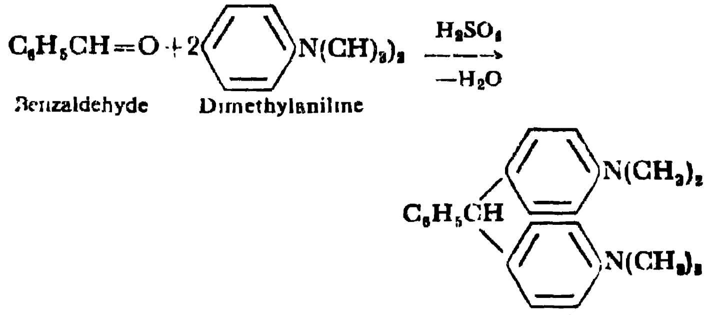
Thus we find that this reaction is similar to aldol condensation (see page 2·197).

(*d*) ***With Aniline.*** Benzaldehyde reacts with primary aromatic amino-compounds to form *anils* or *Schiff's base*, *e.g.*, on warming with aniline, it condenses to give benzylideneaniline.

$$\underset{\text{Benzaldehyde}}{C_6H_5CH=}\boxed{O+H_2}\underset{\text{Aniline}}{N.C_6H_5} \longrightarrow \underset{\text{Benzylideneaniline}}{C_6H_5CH=NC_6H_5}+H_2O \qquad (85\%)$$

Aliphatic aldehydes tend to produce compounds of the type $RCH(NH.C_6H_5)_2$.

(*e*) ***With phenols and tertiary aromatic amines*** in presence of $ZnCl_2$ or H_2SO_4, it condenses to give triphenylmethane derivatives

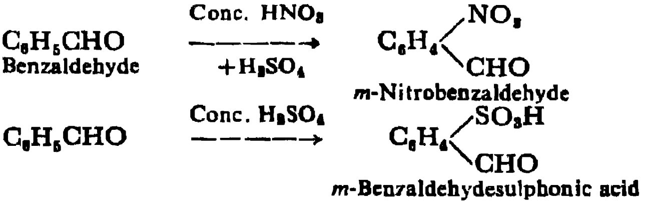


Malachite green

(6) **Action of chlorine.** Benzaldehyde on chlorination in the absence of a halogen carrier gives benzoyl chloride (*cf.*, acetaldehyde). This is because in benzaldehyde there is no α-hydrogen present which could be replaced by chlorine.

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO}+Cl_2 \longrightarrow \underset{\text{Benzoyl chloride}}{C_6H_5COCl} + HCl$$

(7) **Reactions of Benzene Nucleus.** Benzaldehyde can be nitrated and sulphonated as usual, *meta*- derivatives are obtained in each case. Curiously enough, concentrated nitric acid and sulphuric acid mixture does not oxidise benzaldehyde (as expected) but nitrates it.



$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} \xrightarrow[+H_2SO_4]{\text{Conc. }HNO_3} \underset{m\text{-Nitrobenzaldehyde}}{C_6H_4\begin{cases}NO_2\\CHO\end{cases}}$$

$$C_6H_5CHO \xrightarrow{\text{Conc. }H_2SO_4} \underset{m\text{-Benzaldehydesulphonic acid}}{C_6H_4\begin{cases}SO_3H\\CHO\end{cases}}$$

Uses. Benzaldehyde is used (*i*) for flavouring purposes in perfumery ; (*ii*) in the manufacture of dyes ; and (*iii*) for the preparation of organic compounds like cinnamic acid, cinnamaldehyde, benzoyl chloride, etc.

3. Cinnamaldehyde, 3-Phenylpropenal, $C_6H_5CH=CHCHO$. —It is the chief constituent of cinnamon oil from which it can be

separated by preparing the bisulphite compound. Synthetically, it may be prepared from benzaldehyde by Claisen condensation.

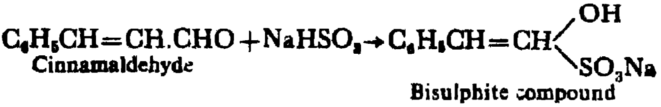
$$\underset{\text{Benzaldehyde}}{C_6H_5CH=}\boxed{O+H_2}\underset{\text{Acetaldehyde}}{CH.CHO}\xrightarrow{NaOH}\underset{\text{Cinnamaldehyde}}{C_6H_5CH=CH.CHO}+H_2O$$

It is a colourless oil (b.p. 525K) which slowly oxidises to cinnamic acid in air on treatment with ammoniacal silver nitrate.

$$\underset{\text{Cinnamaldehyde}}{C_6H_5CH=CH.CHO}+[O]\rightarrow\underset{\text{Cinnamic acid}}{C_6H_5CH=CH.COOH}$$

With vigorous oxidising agents like acid permanganate, the side-chain ruptures at the double bond to produce benzoic acid.

It gives the bisulphite compound with sodium bisulphite but the reaction is reversible.



$$\underset{\text{Cinnamaldehyde}}{C_6H_5CH=CH.CHO}+NaHSO_3\rightarrow\underset{\text{Bisulphite compound}}{C_6H_5CH=CH\left\langle\begin{matrix}OH\\SO_3Na\end{matrix}\right.}$$

With bromine it gives the dibromide by addition of bromine at the double bond.

$$\underset{\text{Cinnamaldehyde}}{C_6H_5CH=CH.CHO}+Br_2\rightarrow\underset{\text{Addition product}}{C_6H_5CHBr-CHBr.CHO}$$

On reduction with aluminium isopropoxide ((*Meerwein-Ponndorf-Verley reagent*), it gives cinnamyl alcohol.

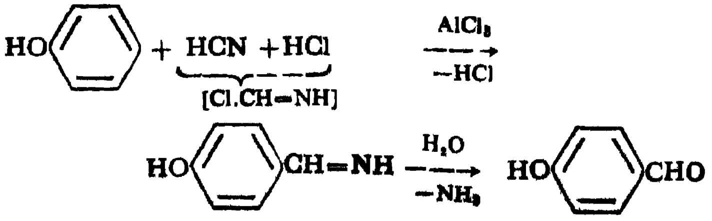
$$\underset{\text{Cinnamaldehyde}}{C_6H_5CH=CH.CHO}+2[H]\xrightarrow{[(CH_3)_2CHO]_3Al}\underset{\text{Cinnamyl alcohol}}{C_6H_5CH=CH.CH_2OH}$$

LiAlH$_4$ and NaBH$_4$ also reduce cinnamaldehyde to cinnamyl alcohol. They reduce the —CHO group but do not reduce the ethylenic double bond.

4. Phenolic Aldehydes or Hydroxyaldehydes.—These are aromatic aldehydes containing one or more hydroxyl groups directly attached to the nucleus.

General Methods of Preparation.

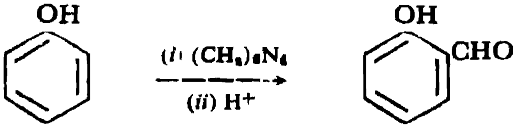
(1) **Gattermann aldehyde synthesis.** *By treating a phenol with a mixture of HCN and HCl in presence of AlCl$_3$ and decomposing the complex produced with water.* *p*-Hydroxybenzaldehyde is obtained as the main product.



(2) **Reimer-Tiemann Reaction** (1876). *By Refluxing an alkaline solution of phenol with chloroform at 330K*. Excess of chloroform is removed by distillation. The residue is acidified with sulphuric acid and steam-distilled when phenol and *o*-hydroxybenzaldehyde distil over and *p*-hydroxybenzaldehyde is left behind.

For mechanism of the reaction see page 2'607.

(3) **Duff's Reaction** (1932). By heating phenol with hexamethylenetetramine, glycerol and boric acid. The mixture is acidified with sulphuric acid and steam-distilled when the *o*-isomer (salicylaldehyde) distils over.



Phenol Salicylaldehyde

Properties of phenolic aldehydes are given under salicylaldehyde, a typical member of the family.

5. Salicylaldehyde (*o*-hydroxybenzaldehyde), $C_6H_4\genfrac{}{}{0pt}{}{OH}{CHO}$

—Salicylaldehyde occurs in certain essential oils. It is prepared—

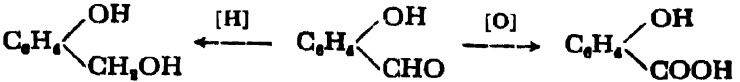
(*i*) *By refluxing an alkaline solution of phenol with chloroform at 360K* **Reimer Tiemann Reaction**, 1876).

For mechanism of the reaction see page 2'607.

The product is acidified with sulphuric acid and steam-distilled when salicylaldehyde and the unchanged phenol distil over leaving behind the *p*-isomer which is also obtained with the *o*-isomer.

(*ii*) **Duff's Reaction**. *See* above.

Salicylaldehyde is a colourless, pleasant-smelling oily liquid (b.p. 470K) soluble in water and alkalis to give a yellow solution. It gives the characteristic reactions of a phenol and an aldehyde, *e.g.*, in aqueous solution, it gives an intense violet coloration with ferric chloride. Salicylic acid is produced on oxidation while *o*-hydroxybenzyl alcohol is obtained on reduction.

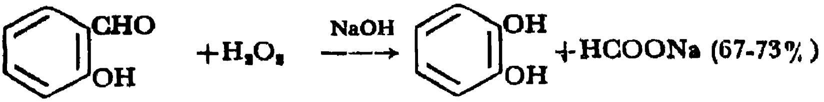


$$C_6H_4\genfrac{}{}{0pt}{}{OH}{CH_2OH} \xleftarrow{[H]} C_6H_4\genfrac{}{}{0pt}{}{OH}{CHO} \xrightarrow{[O]} C_6H_4\genfrac{}{}{0pt}{}{OH}{COOH}$$

o-hydroxybenzyl alcohol Salicylaldehyde Salicylic acid

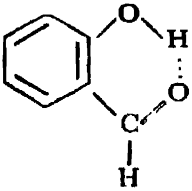
It does not give Schiff's test and does not reduce Fehling's solution. It, however, reduces ammoniacal silver nitrate on prolonged standing.

Salicylaldehyde on oxidation with alkaline hydrogen peroxide gives 1, 2-Benzenediol (**Dakin Reaction,** 1909).



This reaction is characteristic of *o*- and *p*-hydroxyaldehydes.

Hydroxy group in salicylaldehyde is not so reactive as that in the *m*- and *p*-isomers. This is believed to be probably due to intramolecular hydrogen bonding. This also accounts for the fact that salicylaldehyde is steam volatile while *m*- and *p*-isomers are not so.

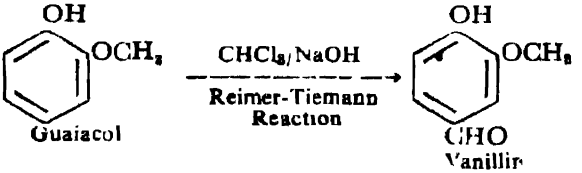


Hydrogen bonding in salicylaldehyde.

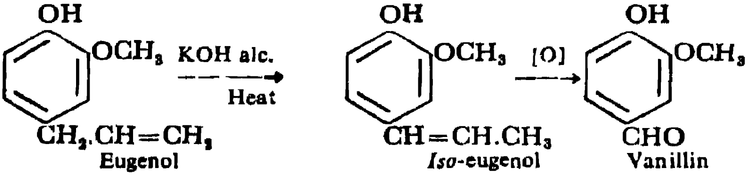
6. **Vanillin, 4-hydroxy-2-methoxybenzaldehyde.**—It occurs in many plant products, *e g.*, the vanilla bean.

Preparation. Vanillin may be prepared—

(*i*) From guaiacol by means of Reimer-Tiemann reaction, or Gattermann reaction (*see* page 2 627).

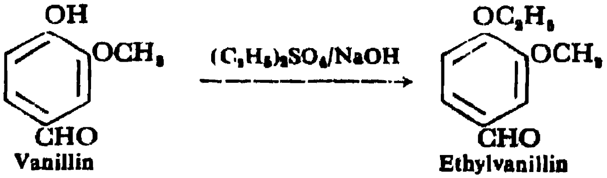


(*ii*) *By oxidation of isoeugenol with nitrobenzene.* Isoeugenol is obtained from eugenol.



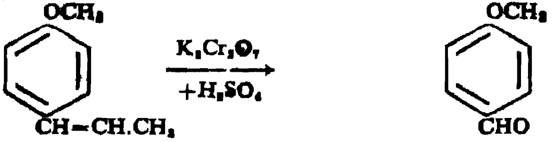
(*iii*) The liquors obtained during extraction of liquid from wood-pulp contain vanillin and are, therefore, used as a source of vanillin.

Properties. It is a pleasant-smelling, colourless, crystalline solid (m.p. 354K). With ferric chloride solution it gives a blue coloration. On heating with HCl it hydrolyses to give protocatechualdehyde. On ethylation it gives ethylvanillin which is three times as strong as vanillin.

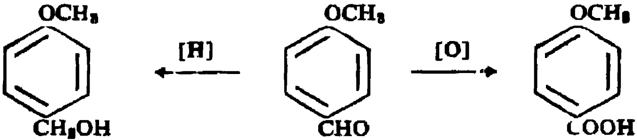


7. **Anisaldehyde,** ***p-methoxy-benzaldehyde.***—It occurs in essential oils. It may be prepared by methylating *p*-hydroxybenzaldehyde or introducing an

aldehyde group in methoxybenzene by Gattermann's aldehyde synthesis. It is, however, manufactured from anethole by ozonolysis or by oxidation with acid dichromate.



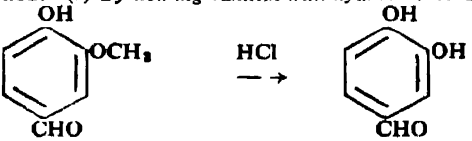
It is an oil (b.p. 521K) which gives anisic acid on oxidation and anisyl alcohol on reduction.



Anisyl alcohol Anisaldehyde Anisic acid

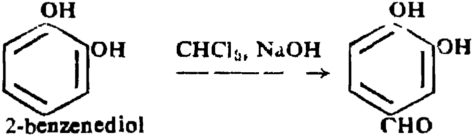
8. **Protocatechualdehyde**, 3, 4-*Dihydroxybenzaldehyde*.

Preparation. (*i*) *By heating vanillin with hydrochloric acid.*



Vanillin Protocatechualdehyde

(*ii*) *From 1, 2-benzenediol by Reimer-Tiemann reaction.*

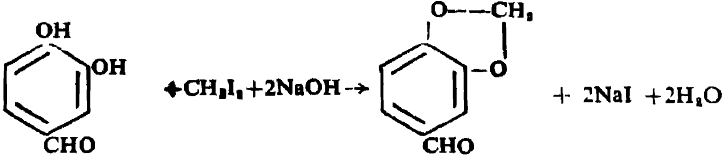


1, 2-benzenediol Protocatechualdehyde

Properties. It is a crystalline solid (m.p. 430K), soluble in water. It produces a green coloration with FeCl$_3$ and reduces ammoniacal silver nitrate solution.

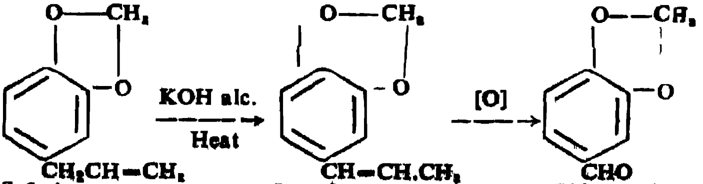
9. **Piperonal**. 3, 4-*methylenedioxobenzaldehyde* — It is the methylene ether of protocatechualdehyde.

Preparation. (*i*) By heating protocatechualdehyde with methylene iodide and sodium hydroxide.



Piperonal

(*ii*) By ozonolysis or oxidation of iso-safrole (obtained from safrole with alc. KOH) with acid dichromate.



Safrole Isosafrole Piperonal

Properties. It is a white solid (m.p. 310K) having the smell of helitrope. On oxidation it forms piperonylic acid while on reduction it gives piperonyl alcohol. On heating with dilute hydrochloric acid at 470K under pressure it yields protocatechualdehyde and formaldehyde or methanol.

10. The Aromatic Ketones.—Aromatic ketones may be :

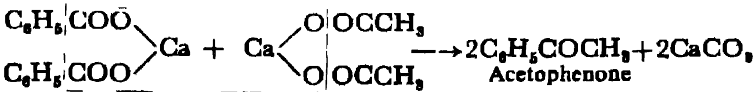
(*i*) *Aromatic-aliphatic or aryl-alkyl ketones* in which one of the two radicals attached to the carbonyl group (>CO) is an aryl radical and the other is an alkyl radical, *e.g.*, acetophenone $C_6H_5CO.CH_3$.

(*ii*) *Purely aromatic or diaryl ketones* in which both the groups attached to the carbonyl group are aryl radicals, *e.g.*, benzophenone or diphenyl ketone, $C_6H_5CO\ C_6H_5$.

In general, aromatic ketones resemble aliphatic ketones except that they do not form bisulphite compounds and give the usual reactions of the benzene nucleus.

11. Acetophenone (Methyl phenyl ketone, Acetylbenzene), $C_6H_5COCH_3$.

Preparation. (1) *By the distillation of a mixture of calcium benzoate and calcium acetate.*



$$(C_6H_5COO)_2Ca + Ca(OOCCH_3)_2 \longrightarrow 2C_6H_5COCH_3 + 2CaCO_3$$

Calcium benzoate Calcium acetate Acetophenone

(2) *By treating benzene with acetyl chloride in presence of anhydrous aluminium chloride* (**Friedel-Crafts Reaction**).

$$C_6H_5\,H + Cl|COCH_3 \longrightarrow C_6H_5COCH_3 + HCl$$

Benzene Acetyl chloride Acetophenone

(3) *By treating benzoyl chloride with dimethylcadmium*

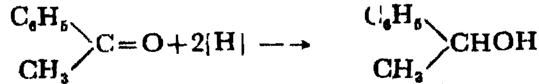
$$2C_6H_5COCl + (CH_3)_2Cd \longrightarrow 2C_6H_5COCH_3 + CdCl_2$$

Dimethylcadmium Acetophenone

Properties : Physical. It is a colourless, crystalline solid (m.p. 293K, b.p. 475K) with a pleasant smell. It is slightly soluble in water.

Chemical. Chemically acetophenone is very similar to acetone For example :

(*i*) **Reduction** On reduction with sodium and ethanol acetophenone gives secondary alcohol (*cf*, acetone ⟶ Isopropyl alcohol).



$$(C_6H_5)(CH_3)C{=}O + 2[H] \longrightarrow (C_6H_5)(CH_3)CHOH$$

Acetophenone Phenylmethylcarbinol

Reduction with amalgamated zinc and concentrated hydrochloric acid (Clemmensen reduction) yields ethylbenzene.

$$C_6H_5COCH_3 + 4[H] \xrightarrow[HCl]{Zn/Hg} C_6H_5CH_2CH_3 + H_2O$$

Acetophenone Ethylbenzene

(*ii*) **Oxidation**. On oxidation with cold $KMnO_4$ it gives *phenylglyoxylic acid* (*benzoylformic* acid), which on further oxidation yields benzoic acid (*cf.*, acetone→acetic acid).

$$C_6H_5COCH_3 \xrightarrow{[O]} C_6H_5COCOOH \xrightarrow{[O]} C_6H_5COOH$$

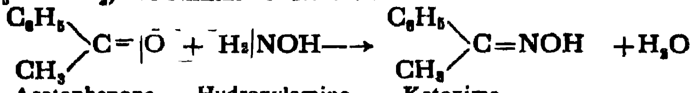
Acetophenone Phenylglyoxylic acid Benzoic acid

On oxidation with selenium oxide, it gives phenylglyoxal.

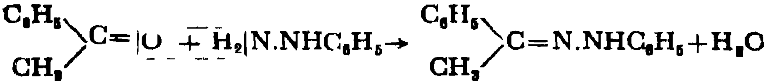
$$C_6H_5COCH_3 + SeO_2 \longrightarrow C_6H_5COCHO + Se + H_2O \ (69\text{-}72\%)$$

Acetophenone Phenylglyoxal

(*iii*) **Condensation Reactions.** Condensation reactions of acetophenone with hydroxylamine (NH_2OH) and phenylhydrazine ($C_6H_5NHNH_2$) are similar to those with acetone.

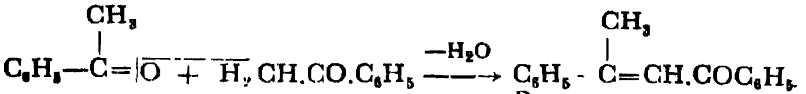


Acetophenone Hydroxylamine Ketoxime



Phenylhydrazone

In presence of aluminium *tert.*-butoxide two molecules of acetophenone condense to give *dypnone.*



$$C_6H_5-\overset{CH_3}{\overset{|}{C}}=O + H_2CH.CO.C_6H_5 \xrightarrow{-H_2O} C_6H_5-\overset{CH_3}{\overset{|}{C}}=CH.COC_6H_5$$

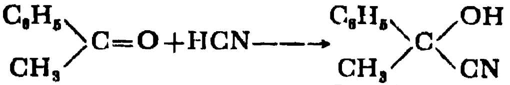
Dypnone

With acetic anhydride it condenses in presence of boron trifluoride etherate to give benzoylacetone.

$$C_6H_5COCH_3 + (CH_3CO)_2O \xrightarrow{BF_3/ether} C_6H_5CO.CH_2COCH_3 + CH_3COOH$$

Benzoylacetone

(*iv*) **Addition reaction** with hydrogen cyanide is similar to that of acetone but with sodium bisulphite there is no reaction.



Cyanohydrin

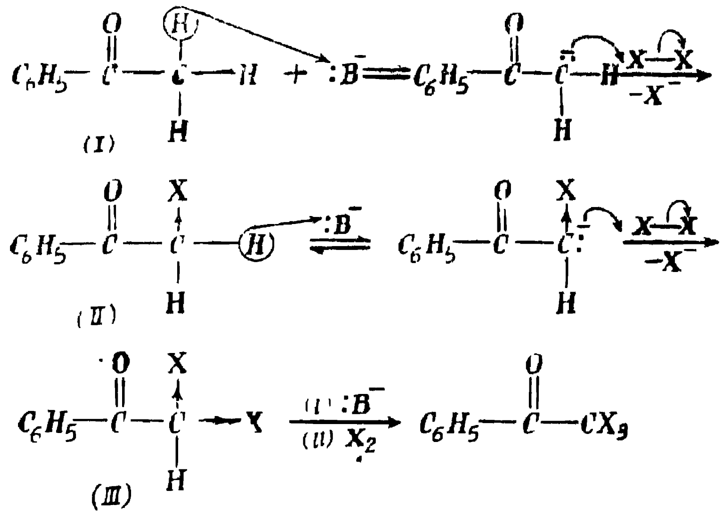
It reacts with ammonia to form acetophenone-ammonia, $(C_6H_5.C.CH_3)_3N_2$ (*cf.*, benzaldehyde which gives hydrobenzamide with ammonia). With Grignard's reagent it reacts as usual similar to acetone.

(*v*) **Halogenation.** Acetophenone is readily halogenated in the ω-position, *e.g.*, on treating it with bromine in ether at 273K. In the presence of a little $AlCl_3$ it gives phenacyl bromide (ω-bromo acetophenone)

$$C_6H_5COCH_3 + Br_2 \longrightarrow C_6H_5COCH_2Br + HBr$$

Acetophenone Phenacyl bromide

(*vi*) **The Haloform Reaction** Like other methyl ketones acetophenone reacts with halogens in the presence of base (*i e.*, in hypohalite solutions) when three hydrogen atoms of the methyl group are replaced by halogen atoms. Multiple halogenation occurs because on substitution of the first hydrogen by halogen atom, the remaining hydrogens on methyl carbon are more acidic through inductive effect of halogen atom. Thus H atom of CH_3 in I is acidic but the H atom of CH_2X in II is more acidic due to inductive effect of X atom. For the same reason H atom of CHX_2 in III is most acidic.



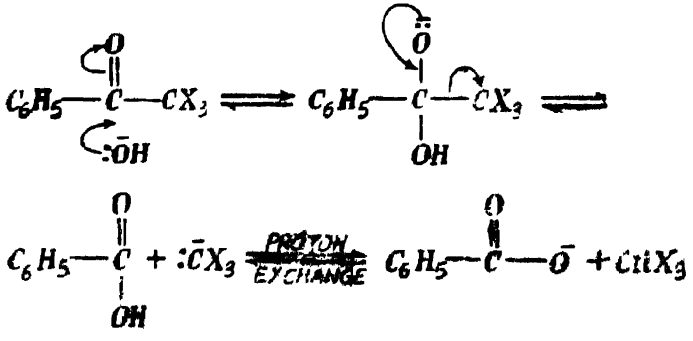
This is an example of base promoted halogenation. Different steps involved are :

(*i*) Abstraction of a proton by the base $:\bar{B}$.

(*ii*) Electrophilic attack by the halogen at the negatively charged centre.

(*iii*) Repetition of the above two steps till all the three hydrogen atoms of the CH_3 group are replaced by three halogen atoms.

The trihaloketone so obtained further reacts with aqueous alkali. The OH^- attacks the carbon atom of the trihaloketone and causes a cleavage of the carbon-carbon bond between the carbonyl group and the trihalomethyl group. The ultimate products are the benzoate ion and the haloform ($CHCl_3$, $CHBr_3$ or CHI_3)

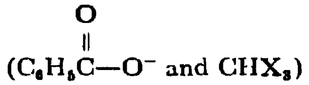


Various steps involved in the mechanism of the reaction are :

(*i*) Nucleophilic attack by $:\bar{O}H$.

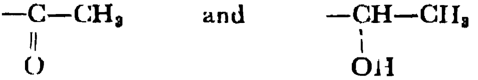
(*ii*) Adduct loses $:\bar{C}X_3$ to form benzoic acid.

(*iii*) Proton exchange to form a more stable pair



$$(C_6H_5\overset{\overset{\displaystyle O}{\|}}{C}—O^- \text{ and } CHX_3)$$

The haloform reaction using iodine and aqueous NaOH is termed the iodoform reaction. It is given by all compounds containing the two groups shown below :



$$—\underset{\underset{\displaystyle O}{\|}}{C}—CH_3 \qquad \text{and} \qquad —\underset{\underset{\displaystyle OH}{|}}{CH}—CH_3$$

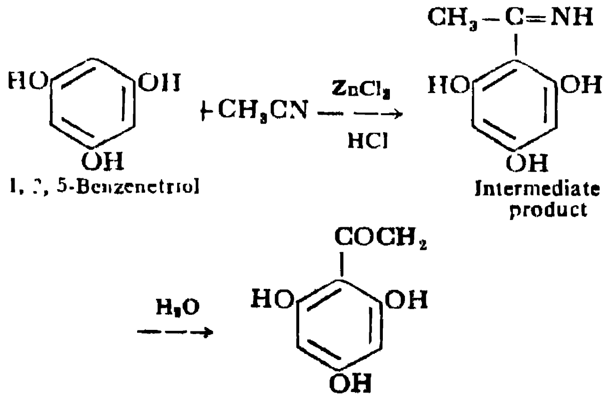
(*vii*) **Reactions of the Benzene Nucleus.** Unlike aliphatic ketones, acetophenone can be nitrated and sulphonated, meta derivative is obtained in each case.

Uses. (*i*) As hypnotic (sleep-producing drug) in medicine under the name *hypnone*.

(*ii*) In perfumery.

12 **Phenolic Ketones.**—A number of phenolic ketones occur in nature free or as glycosides. These may be prepared—

(*i*) **By Houben-Hoesch Synthesis** (*1927*). *By condensation of cyanides with polyhydric phenols (m-isomers particularly) in presence of $ZnCl_2$ and HCl.* For example, 1, 3, 5-Benzenetriol condenses with methyl cyanide to form 2, 4, 6 Trihydroxy-acetophenone



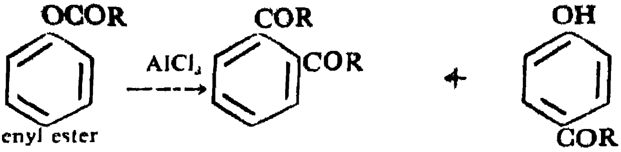
1, 3, 5-Benzenetriol

Intermediate product

2, 4, 6-Trihydroxy-acetophenone

Houben-Hoesch synthesis is only an extension of Gattermann's phenolic aldehyde synthesis. It is not applicable to phenol itself.

(ii) ***By Fries Rearrangement.*** A phenyl ester on treatment with anyhydrous $AlCl_3$ gives *o*- or *p*-hydroxyketone or a mixture of both.



Phenyl ester

ortho- and para-
hydroxyphenyl ketones

13. Benzophenone (Diphenyl ketone), $C_6H_5.COC_6H_5$

Preparation (1) *By heating calcium benzoate*

$$(C_6H_5COO)_2Ca \longrightarrow C_6H_5.COC_6H_5 + CaCO_3 \qquad (30\%)$$

(2) *By Friedel-Crafts reaction between benzene and benzoyl chloride.*

$$C_6H_6 + C_6H_5COCl \xrightarrow{AlCl_3} C_6H_5COC_6H_5 + HCl \qquad (80\%)$$

Instead of benzoyl chloride, carbonyl chloride may be used.

$$2C_6H_6 + COCl_2 \xrightarrow{AlCl_3} C_6H_5\,CO.C_6H_5 + HCl$$

3 Commercially benzophenone is obtained by Friedel-Crafts reaction between benzene and carbon tetrachloride followed by steam-distillation of the dichloro-compound obtained.

$$2C_6H_6 \quad CCl_4 \xrightarrow[-2HCl]{AlCl_3} (C_6H_5)_2CCl_2 \xrightarrow[-\,2HCl]{H_2O} (C_6H_5)_2CO \qquad (80\text{-}89\%)$$

Properties It is a colourless, pleasant-smelling solid and exists in two forms, a stable form (m.p. 322K) and an unstable form (m.p 299K). It is insoluble in water but soluble in alcohol or ether

It shows the characteristic properties of the keto group but forms no bisulphite compound, *e g*, on reduction with sodium amalgam it gives benzhydrol or diphenylcarbinol, a secondary alcohol.

$$\underset{\text{Benzophenone}}{(C_6H_5)_2CO} + 2[H] \longrightarrow \underset{\text{Benzhydrol}}{(C_6H_5)_2CHOH}$$

When distilled with zinc dust or when treated with amalgamated zinc and concentrated hydrochloric acid (*Clemmensen reduction*) benzophenone is reduced to diphenylmethane, $(C_6H_5)_2CH_2$.

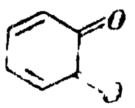
$$C_6H_5COC_6H_5 + 4[H] \xrightarrow[HCl]{Zn/Hg} \underset{\text{Diphenylmethane}}{C_6H_5CH_2C_6H_5} + H_2O$$

On fusion with solid caustic potash it breaks to give benzene and benzoic acid.

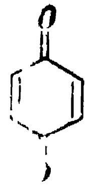
$$\underset{\text{Benzophenone}}{C_6H_5COC_6H_5} + KOH \xrightarrow{Fuse} C_6H_6 + \underset{\text{Pot benzoate}}{C_6H_5COOK}$$

QUINONES

14 Benzoquinones.—Benzoquinones are unsaturated cyclic diketones formed by the replacement of two hydrogen atoms by two oxygen atoms. Two benzoquinones are known. These are :



o-Benzoquinone

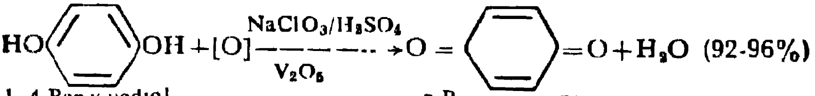


p-Benzoquinone

m-Benzoquinone is not known. It is not possible to construct a similar formula with two carbonyl groups in the *m*-position and at the same time maintaining a valency for carbon.

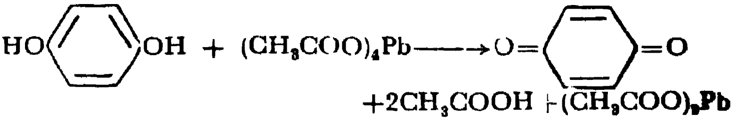
15. *p*-Benzoquinone (*p-quinone*) —It is the most important member of the family and is commonly referred to simply as quinone.

Preparation. (*i*) *By oxidation of* 1, 4 Benzenediol with ferric chloride, manganese dioxide and sulphuric acid, dichromate; or sodium chlorate in dilute sulphuric acid in the presence of V_2O_5 (*catalyst*) The last named oxidising agent is the best

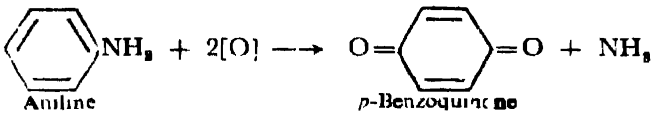


1, 4 Benzenediol p-Benzoquinone

(*ii*) *By oxidation of 1, 4 Benzenediol with lead tetraacetate*



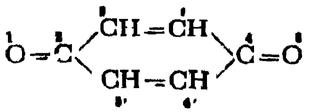
(*iii*) *By oxidation of aniline with potassium dichromate and sulphuric acid* (**Laboratory method**).



Aniline p-Benzoquinone

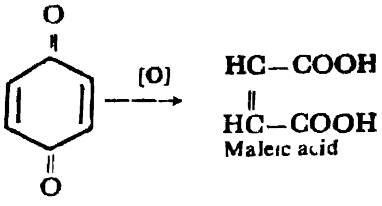
Properties. *p*-Benzoquinone crystallizes as yellow prisms (m p. 389K) with a sharp odour It sublimes on heating and is volatile in steam It is slightly soluble in water but dissolves readily in alcohol and ether. On exposure to light it turns brown.

It has a *crossed conjugated system* with three conjugated double bonds not arranged in a continuous straight chain



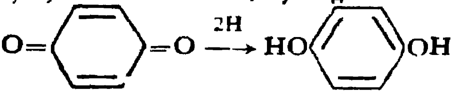
It behaves like an αβ-unsaturated ketone rather than as an aromatic compounds as shown by its chemical properties given below;

(*i*) **Oxidation.** With silver peroxide it is oxidised to maleic acid.



p-quinone

(*ii*) **Reduction.** It is easily reduced to 1, 4-benzenediol (1 : 6-addition) by sulphurous acid, hydrogen or sodium hyposulphite.

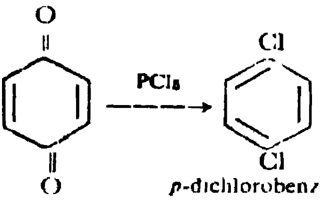


(80%)

p-quinone Quinol

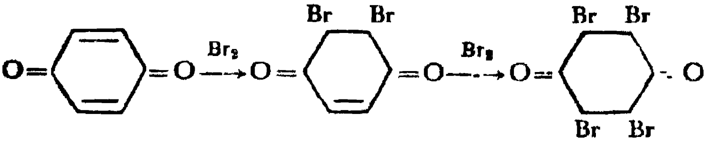
Here the >C=O group does not get reduced to the group >CHOH. Instead of this it gives the groups ≡COH and quinone ring reverts back to the benzene structure.

(*iii*) **With PCl$_5$** It reacts with phosphorus pentachloride to give *p*-dichlorobenzene. Here also each oxygen atom is replaced only by one Cl atom (not two as expected) and quinone ring reverts to the benzene structure.



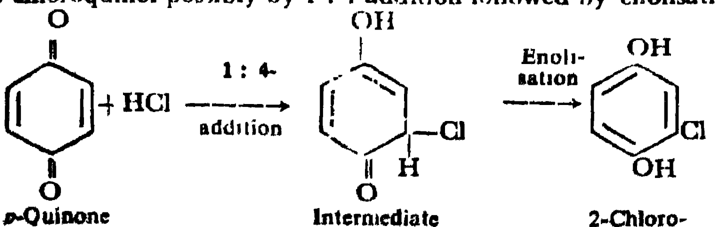
p-dichlorobenzene

(*iv*) **Addition of Halogens.** With bromine it gives dibromo-derivative (by 3,4-addition) With excess of bromine it adds two more bromine atoms (in 3′ 4′-positions) to form the tetrabromo derivative.



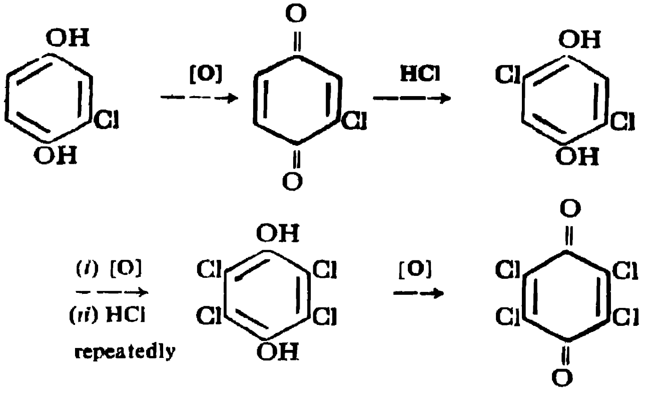
p-quinone Dibromo-derivative Tetrabromo-derivative

(*v*) **With Hydrochloric acid** It adds one molecule of HCl to give chloroquinol possibly by 1 : 4-addition followed by enolisation.



p-Quinone Intermediate product 2-Chloro-1, 4-benzenediol

On oxidation, 2-chloro-1, 4-benzenediol yields chloro-*p*-benzoquinone. By repeating the process of adding HCl followed by oxidation each time, we get chloranil (tetrachloro-*p*-benzoquinone).

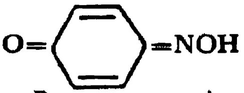


Chloranil

(*vi*) **Chlorination.** Halogens give addition or substitution products with quinone depending upon the experimental conditions. For example, chlorination gives chloranil, a substitution product.

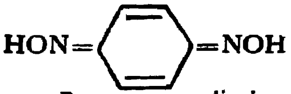
(*vii*) **Oxidising property.** Because of its easy reduction to quinol, *p* benzoquinone is a fairly strong oxidising agent. Presence of electron-attracting groups increases its oxidising power. Thus chloranil is a stronger oxidising agent and a fungicide.

(*viii*) **With Hydroxylamine.** Quinone reacts with hydroxylamine to form oxime and dioxime. This shows the presence of two carbonyl groups.



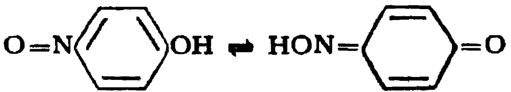
Benzoquinone-oxime

and



Benzoquinone-dioxime

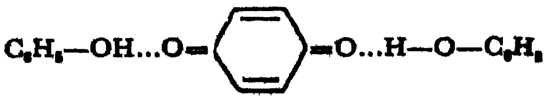
The monoxime resembles *p*-nitrosophenol and gives *p*-nitrophenol on oxidation. This shows that the two compounds are tautomeric.



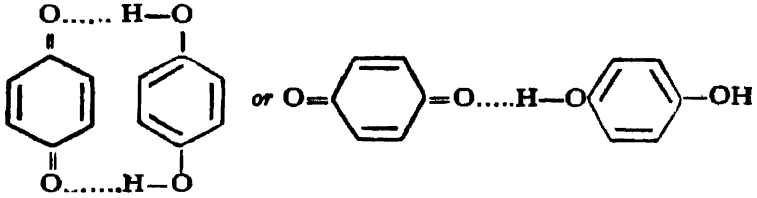
p-nitrosophenol   Quinone-oxime

(*ix*) **Formation of Addition Compounds.** It forms addition compounds of uncertain structures with a number of aromatic compounds. For example,

(*a*) With phenol it gives phenoquinone, a complex formed by hydrogen bonding. This may be



(b) Quinhydrone is a green crystalline compound believed to be a complex formed by hydrogen bonding between one molecule of *p*-quinone and one of 1, 4-benzenediol.



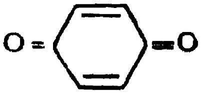
Quinhydrone is used in the measurement of hydrogen-ion concentration by the potentiometric method.

16. Structure of *p*-benzoquinone.—(*a*) Molecular formula of *p*-benzoquinone as deduced from its analytical data and mol. wt. determination is $C_6H_4O_2$.

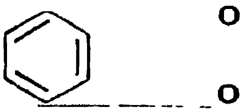
(*b*) *Fittig's formula.* (*i*) *p*-Benzoquinone on reduction gives 1, 4-benzenediol. This shows that in *p*-benzoquinone the two oxygen atoms are in *p*-positions.

(*ii*) This view is further supported by the fact that 1, 4-benzenediol on mild oxidation gives *p*-benzoquinone.

(*iii*) Keeping these facts in view Fittig proposed the following formula for *p*-benzoquinone :



(*c*) *Graebe's formula* Fittig's structure does not agree with certain other properties of *p*-benzoquinone. For example, on treatment with PCl_5 it gives *p*-dicholorobenzene. This suggests that the two oxygen atoms are linked to the two carbon atoms by single bonds. Graebe (1867) suggested the following formula for it :



This is supported by the fact that *p*-benzoquinone is a strong oxidising agent like hydrogen peroxide, the structure of which is H—O—O—H.

(*d*) Many other properties of *p*-benzoquinone support Fittig's formula and do not agree with Graebe's formula. For example :

(*i*) It gives monoxime and dioxime which suggests the presence of two carbonyl groups.

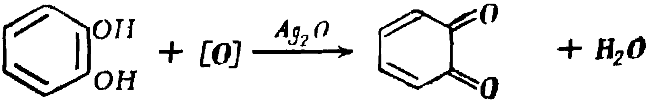
(*ii*) It behaves as an unsaturated cyclic ketone rather than an aromatic compound as shown by addition of halogens and halogen acids.

(*iii*) Infra-red spectrum shows the presence of carbonyl groups.

(*iv*) If Graebe's formula were correct, there appears to be no reason why *m*-benzoquinone should not exist.

From the above discussion it is clear that Fittig's formula agrees better with the properties of *p*-benzoquinone and is, therefore, accepted as its structural formula.

17. **o-Bezoquinone or o-Quinone.**—It is prepared by the oxidation of 1, 2-benzenediol with silver oxide.



1, 2-benzenediol o-Benzoquinone

o-Benzoquinone is readily oxidised by silver oxide in presence of water. Anhydrous sodium sulphate is, therefore, added to remove water.

It exists in two forms :

(*i*) Green needles (*unstable*).

(*ii*) Light red crystalline plates (*stable*).

It is odourless and not volatile in steam. It is reduced to catechol with sulphurous acid. It is a strong oxidising agent and liberates iodine from acidified potassium iodide.

QUESTIONS

A. Essay Type :

1. How is benzaldehyde prepared from toluene ? Give at least five important reactions of the compound. Show how it differs from acetaldehyde.
(*Delhi B.Sc. Hons. Sub. 1976 Supp.* ; *Jabalpur B.Sc. 1973*)

2. Give two important methods of obtaining salicylaldehyde. Compare and contrast its reactions with those of benzaldehyde.
(*Delhi B.Sc. Hons. Sub. 1977* ; *Delhi B.Sc. 1976*)

3. Describe the preparation of Acetophenone. How can you obtain the following from it :

(*i*) Benzoic acid, (*ii*) Phenacyl bromide, (*iii*) Dypnone, (*iv*) Benzoyl acetone ? (*Rajasthan B.Sc. 1971*)

4. Give the preparation and properties of any two of the following :

(*i*) Benzophenone ; (*ii*) Vanillin ; (*iii*) Protocatechualdehyde ; (*iv*) Piperonal. (*Kerala B.Sc. 1973*)

5. What is quinone ? Describe two methods of preparing *p*-benzoquinone. Discuss its important physical and chemical properties. Would you include these compounds under aromatic class ? Give reasons.

6. Write short notes on :

(*i*) Rosenmund's reaction. (*ii*) Etard's reaction.

(*iii*) Gattermann-Koch aldehyde synthesis.

(*iv*) Gattermann aldehyde synthesis (*v*) Stephen's reaction.

(*vi*) Sommelet reaction. (*vii*) Tischenko reaction.

(*viii*) Crossed Cannizzaro reaction. (*ix*) Reimer-Tiemann reaction.

(*x*) Houben-Hoesch synthesis. (*xi*) Fries rearrangement.

7. How will you distinguish between :

(i) Benzaldehyde, benzophenone and acetophenone,

(ii) *n*-Valeraldehyde and benzaldehyde, and

(iii) Salicylaldehyde and *p*-hydroxybenzaldehyde ?

8. How will you prepare :

(*a*) *p*-Tolualdehyde from (*i*) *p*-toluic acid, and (*ii*) *p*-toluonitrile,

(*b*) Phenylethylamine from acetophenone,

(*c*) *p*-Bromoacetophenone from bromobenzene and acetic anhydride,

(*d*) Benzil from benzaldehyde,

(*e*) Benzaldehyde from benzene ?

B. Short Answer Type :

1. Complete the following equations and give the name of the reaction involved in each case :

(*i*) $C_6H_5CHO + CH_2(COOH)_2 \xrightarrow{\text{Pyridine}}$

(*ii*) $C_6H_5CHO + (CH_3CO)_2O \xrightarrow{CH_3COONa}$

(*Delhi B.Sc. Hons. Sub 1977*)

2. Discuss mechanism involved in the following reactions :

(*i*) Benzaldehyde is heated with sodium propionate and propionic anhydride.

(*ii*) Benzaldehyde is refluxed with aqueous ethanolic potassium cyanide.

(*Delhi B.Sc. Hons. 1977*)

3. How is cinnamic acid prepared ? How does it react with : (*i*) ammoniacal silver nitrate, (*ii*) Br_2, (*iii*) $NaHSO_3$ and (*iv*) aluminium isopropoxide ?

4. Give two methods for the preparation of salicylaldehyde.

5. Give one example to illustrate each of the following :

(*i*) Wittig reaction

(*ii*) Reductive amination. (*Punjab B.Sc. 1975*)

6. Complete the following reactions, indicating against each the name of the reaction involved :

(*i*) $C_6H_5COCH_3 \xrightarrow{NaIO}$

(*ii*) $Me_3CCHO + HCHO \xrightarrow{OH^-}$

(*iii*) $C_6H_5CHO + (CH_3CH_2CO)_2O \xrightarrow{CH_3CH_2COONa}$

(*Punjab B.Sc. 1976*)

7. The reactions of aldehydes and ketones with $LiAlH_4$ and $NaBH_4$ are examples of nucleophilic additions to the carbonyl group ($>C=O$). Name the nucleophile involved in the reactions.

8. Why is the first step in halogenation of acetophenone in aqueous NaOH solution termed "base promoted" rather than base catalyzed ?

9. Which of the following compounds would give a positive iodoform test ?

(*i*) Acetophenone
(*ii*) Acetone
(*ii*) 2-Pentanone
(*iv*) 3-Pentanone
(*v*) 1-Phenylethanol
(*vi*) 2-Phenylethanol
(*vii*) 2-Butanol
(*viii*) 3-Pentanol
(*ix*) Acetaldehyde
(*x*) Benzaldehyde

10. Give a suitable mechanism for each of the following :

(*a*) Perkin's reaction (*b*) Cannizzaro reaction

(*c*) Benzoin condensation (*d*) Knoevenagel reaction

(*e*) Claisen-Schmidt reaction

(Kurukshetra B.Sc. 1978 Supp., 78 ; Delhi 1978 ; Madras 1978)

11. How will you obtain (*i*) Benzylideneaniline and (*ii*) Cinnamic acid from benzaldehyde ? *(Kurukshetra B.Sc. 1977 Supp.)*

12. How will you convert benzaldehyde into 3-phenylpropionic acid ? *(Kurukshetra B.Sc. 1974)*

13. How is benzaldehyde prepared ? Give reactions in which it differs from acetaldehyde. *(Delhi B.Sc. 1978)*

14. What is the order of reactivity of benzaldehyde, benzophenone and acetophenone towards nucleophilic addition reactions ? Explain. *(Guru Nanak Dev B.Sc. 1977)*

15. How will you obtain ethylbenzene, benzoic acid and benzoylacetone from acetophenone ? *(Guru Nanak Dev B.Sc. 1977)*

16. Why carbonyl compounds have lower boiling points than the alcohols from which they are derived ? *(Guru Nanak Dev B.Sc. 1977)*

17 How does benzaldehyde react with a solution of sodium hydroxide ?

(*i*) Mention the name of the above reaction

(*ii*) Give two examples of other aldehydes which undergo a similar reaction.

(*iii*) Give the mechanism of the reaction involved.

(Delhi B.Sc. Hons. 1980)

18. Discuss the mechanism of Claisen condensation. *(Osmania B.Sc. 1980)*

C. Problems :

1. An organic compound having 79·85% of carbon and 5·66% of hydrogen had the vapour density 53. It had a characteristic smell and on oxidation with potassium permanganate, it gave an acid the sodium salt of which on distillation with soda-lime gave benzene. What is the original compound ?

2. A compound (A) contains 80% carbon and 6·7% hydrogen. On oxidation it yields an acid (B) which contains 68·8% carbon and 4·9% hydrogen. (A) reacts with hydroxylamine to give (M) containing 71·1% carbon, 6·7%, hydrogen and 10·4% nitrogen. When (M) is reduced, an amine results which can be resolved into optical isomers. What is the structure of (A) ?

3. An organic compound (X) containing C=68·84% ; H=4·92% and O=26·24% and a vapour density of 61, reacts with hydroxylamine to give a compound (Y).

(Y) on treatment with acetic anhydride gives anoher compound (Z) which when reacted with caustic potash gives ammonia and *m*-hydroxybenzoic acid.

Again the compound (Y) when treated with sodium and alcohol gives a compound (Z′) which with nitrous acid gives another one (Z″). On oxidation (Z″) gives *m*-hydroxybenzoic acid.

Name the compounds (X), (Y), (Z), (Z′) and (Z″) and explain the above changes. How is (X) synthesised ?

ANSWERS AND HINTS

A. 7. (*i*) C_6H_5CHO has characteristic smell of bitter almonds and the other two have a pleasant smell. Acetophenone gives Iodoform reaction, benzophenone does not.

(*ii*) Benzaldehyde does not reduce Fehling's solution, valeraldehyde does.

(*iii*) Salicylaldehyde is steam-volatile, the other is not.

6. (*a*) (*i*) —COOH → —COCl → —CHO (*By* Rosenmund's *reaction*)

(*ii*) —CN ⟶ CHO (Stephen's reaction).

(*b*) $>C=O \longrightarrow$ oxime $\longrightarrow$ Reduction.

(*c*) Friedel-Crafts reaction.

(*d*) C_6H_5CHO+aq. alc. KCN ⟶ *Benzoin* ⟶ *oxidation by* HNO_3 ⟶ *Benzil.*

(*e*) *Gattermann-Koch aldehyde synthesis or Gattermann aldehyde synthesis.*

B. 7. Hydride ion (H^-).

8. Since base is actually consumed during this step.

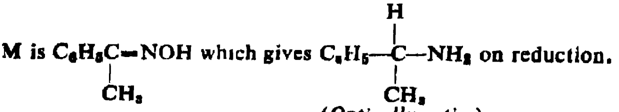
9. (*i*), (*ii*) (*iii*), (*v*), (*vii*) and (*ix*)

12. $C_6H_5CHO \rightarrow$ cinnamic acid by Perkin reaction → reduction

14. $C_6H_5CHO > C_6H_5COCH_3 > C_6H_5COC_6H_5$

C. 1. C_6H_5CHO (Benzaldehyde).

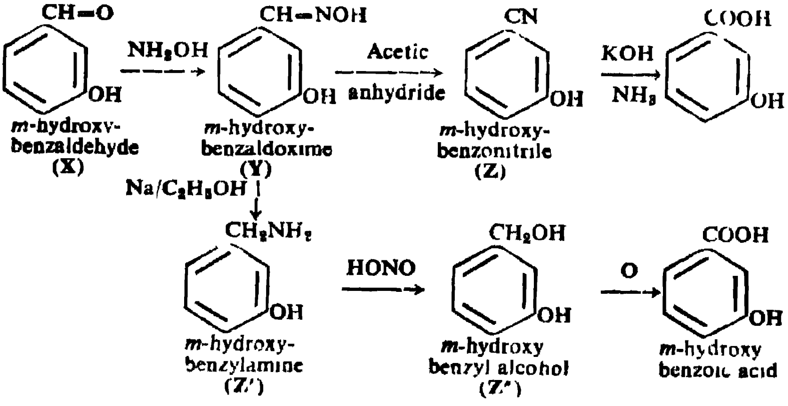
2. A is $C_6H_5COCH_3$ (*Acetophenone*) ; B is C_6H_5COOH (*Benzoic acid*) :



M is $C_6H_5\underset{\displaystyle CH_3}{\underset{|}{C}}{=}NOH$ which gives $C_6H_5{-}\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}{-}NH_2$ on reduction.

(*Optically active*)

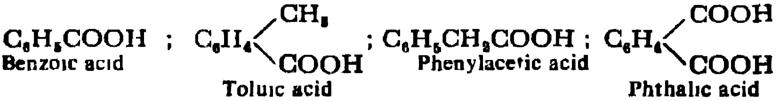
3.



44

Aromatic Acids

1. **Introductory.**—The aromatic acids are derived from aromatic hydrocarbons by the replacement of one or more hydrogen atoms by carboxyl groups (—COOH) which are directly attached to the nucleus. The acids containing the carboxyl group in the side-chain may be regarded as aryl-substituted aliphatic acids. But they are also classified as aromatic acids because of their aromatic character due to the presence of a benzene ring. Some typical aromatic acids are :



C_6H_5COOH ; $C_6H_4\begin{smallmatrix}CH_3\\COOH\end{smallmatrix}$; $C_6H_5CH_2COOH$; $C_6H_4\begin{smallmatrix}COOH\\COOH\end{smallmatrix}$

Benzoic acid ; Toluic acid ; Phenylacetic acid ; Phthalic acid

MONOBASIC ACIDS WITH CARBOXYL GROUP ATTACHED TO THE NUCLEUS

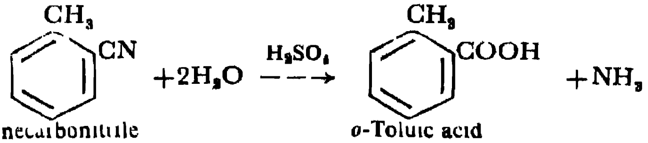
2. **General Methods of Preparation.**—General methods for the preparation of aromatic acids are :

(*i*) *By the oxidation of corresponding alcohol or aldehyde, e.g.*, benzyl alcohol or benzaldehyde gives benzoic acid.

$$\underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} \xrightarrow[O]{KMnO_4} \underset{\text{Benzaldehyde}}{C_6H_5CHO} \xrightarrow[O]{KMnO_4} \underset{\text{Benzoic acid}}{C_6H_5COOH} \qquad ((\imath.g\,)$$

(*ii*) *By the hydrolysis of aromatic nitriles, e.g.*, benzonitrile on hydrolysis gives benzoic acid and *o*-toluenecarbonitrile gives *o*-toluic acid

$$\underset{\text{Benzonitrile}}{C_6H_5CN} + 2H_2O \xrightarrow{H_2SO_4} \underset{\text{Benzoic acid}}{C_6H_5COOH} + NH_3 \qquad (g.\text{-}v.g.)$$



o-Toluenecarbonitrile *o*-Toluic acid

The nitrile may be obtained *by fusing the alkali salt of sulphonic acid with potassium cyanide.*

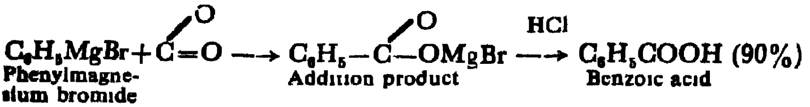
$$C_6H_5\boxed{SO_3K + K}CN \longrightarrow C_6H_5CN + K_2SO_3$$

Or

By Sandmeyer's reaction, i.e., by treating a diazotised amino-compound with cuprous cyanide dissolved in aqueous potassium cyanide.

$$C_6H_5N_2Cl \xrightarrow{K_3Cu(CN)_4} C_6H_5CN + N_2$$

(iii) By means of Grignard reagent, phenylmagnesium bromide with CO_2 yields benzoic acid.



(*iv*) *By Friedel-Crafts reaction, e.g.*, when benzene is treated with excess of carbonyl chloride in the presence of anhydrous aluminium chloride, benzoyl chloride is produced. This on hydrolysis gives benzoic acid. The yield is about 55-58%.

$$C_6H_6+COCl_2 \xrightarrow{AlCl_3} \underset{\text{Benzoyl chloride}}{C_6H_5COCl} \xrightarrow{H_2O} \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

Excess of carbonyl chloride is necessary as otherwise benzophenone may be obtained as the main product.

(*v*) *By the oxidation of homologues of benzene* with dilute nitric acid, dichromate+sulphuric acid, alkaline permanganate, etc. Sometimes it may be more convenient to chlorinate the hydrocarbon and then oxidise the chloro derivative.

$$\underset{\text{Toluene}}{C_6H_5CH_3} \xrightarrow{Cl_2} \underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} \xrightarrow[KMnO_4]{Na_2CO_3} \underset{\substack{\text{Benzyl alcohol}\\ \textit{(Intermediate product)}}}{C_6H_5CH_2OH}$$

$$\xrightarrow{[O]} \underset{\text{Benzoic acid}}{C_6H_5COOH} \qquad (80\%)$$

Oxidation of side-chain *via* chlorination is very easy since the intermediate alcohol is comparatively more readily oxidised than the original hydrocarbon

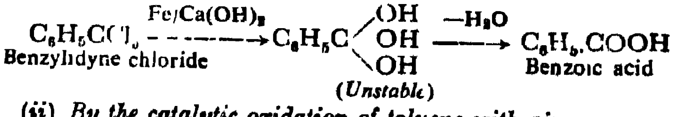
3. **General Properties** —As compared with aliphatic acids the aromatic acids are less volatile, less soluble in water and slightly stronger acids in general. This is because phenyl group, like a double bond, exerts an electron-withdrawing effect on the carboxyl group. When heated with soda-lime these are readily decarboxylated. Their more important reactions are given under benzoic acid.

4 **Benzoic acid (Benzenecarboxylic acid), C_6H_5COOH.—.** Benzoic acid is found in balsams and resins particularly gum benzoin. It is also present as *hippuric acid* (*benzylglycine*) in the urine of horses.

Preparation Benzoic acid can be prepared in the laboratory by any of the general methods of preparation given above.

Manufacture. Commercial benzoic acid is prepared :

(*i*) *By the hydrolysis of benzylidyne chloride* with milk of lime in the presence of iron powder (catalyst).



(*ii*) *By the catalytic oxidation of toluene with air.*

$$\underset{\text{Toluene}}{2C_6H_5.CH_3}+3O_2 \longrightarrow \underset{\text{Benzoic acid}}{2C_6H_5.COOH}+2H_2O$$

(*iii*) ***By means of Friedel-Crafts reaction between benzene and carbonyl chloride and hydrolysis of benzoyl chloride obtained.***

$$C_6H_6+\underset{\text{Carbonyl chloride}}{COCl_2} \longrightarrow \underset{\text{Benzoyl chloride}}{C_6H_5COCl} \longrightarrow \underset{\text{Benzoic acid}}{C_6H_5COOH} \quad (55\text{-}58\%)$$

Properties : Physical. Benzoic acid forms white, pearly flakes (m.p. 395K), sparingly soluble in cold water but readily soluble in hot water, alcohol and ether. It is volatile in steam, and sublimes when heated at about 375K. Its vapours are irritating in smell and provoke coughing and sneezing.

Chemical. Chemically benzoic acid resembles aliphatic acids and gives similar reactions. It is, however, a stronger acid than acetic acid.

(*a*) **Reactions of Carboxyl group :**

(*i*) Salts are produced by neutralization, when benzoic acid reacts with an alkali hydroxide or carbonate.

$$C_6H_5COOH+NaOH \longrightarrow \underset{\text{Sodium benzoate}}{C_6H_5COONa}+H_2O$$

(*ii*) Benzoic acid readily forms esters when it is refluxed with alcohol in the presence of small quantity of concentrated sulphuric acid or hydrogen chloride.

$$\underset{\text{Benzoic acid}}{C_6H_5CO|OH} + \underset{\text{Ethanol}}{H|OC_2H_5} \xrightarrow{\text{Conc. } H_2SO_4} \underset{\text{Ethyl benzoate}}{C_6H_5COOC_2H_5}+H_2O$$

(*iii*) With phosphorus pentachloride it gives benzoyl chloride.

$$\underset{\text{Benzoic acid}}{C_6H_5COOH}+PCl_5 \longrightarrow \underset{\text{Benzoyl chloride}}{C_6H_5COCl}+POCl_3+HCl$$

(*iv*) When heated with soda-lime, benzoic acid gives benzene.

$$C_6H_5COOH+CaO \longrightarrow C_6H_6+CaCO_3$$

(*v*) With ammonia it gives ammonium benzoate which on heating gives benzamide.

$$\underset{\text{Benzoic acid}}{C_6H_5COOH} \xrightarrow{NH_3} \underset{\text{Amm. benzoate}}{C_6H_5COONH_4} \xrightarrow{\text{Heat}} \underset{\text{Benzamide}}{C_6H_5CONH_2}$$

(*b*) **Reactions of the Phenyl group :**

Benzoic acid gives the usual substitution reaction of the nucleus, *e.g.*, nitration, sulphonation and halogenation. The meta derivative is obtained in each case.

Uses. (*i*) The acid and some of its salts are used in medicine as urinary antiseptic

(*ii*) Sodium benzoate finds use as food preservative.

(*iii*) The acid is also used in the manufacture of aniline blue—a dyestuff.

(*iv*) Its vapours mixed with steam are inhaled for disinfecting bronchial tubes.

Tests. (*i*) Benzoic acid dissolves in hot water but separates again on cooling as shining white flakes.

(*ii*) It liberates carbon dioxide from a warm solution of sodium carbonate.

(*iii*) When fused with soda-lime, inflammable vapours of benzene are evolved.

(*iv*) A neutralized solution of benzoic acid gives a buff-coloured precipitate with ferric chloride.

(*v*) On warming with alcohol and conc. H_2SO_4, a characteristic sweet smell of ethyl benzoate is perceived.

5. Comparison between Benzoic acid and Phenol.

Points of Similarity :

(*i*) Both are acidic in nature—turn blue litmus red and neutralize alkalis.

(*ii*) Both liberate hydrogen with metallic sodium.

(*iii*) Both react with PCl_5—phenol yields chlorobenzene while benzoic acid gives benzoyl chloride.

(*iv*) Both give the usual substitution reactions of the benzene nucleus, *e.g.*, nitration, sulphonation and halogenation.

Points of Difference :

(*i*) Phenol is a weaker acid and does not decompose carbonates.

(*ii*) Phenol gives a violet colour with ferric chloride solution while benzoic acid gives only a buff-coloured precipitate.

(*iii*) Phenolic group (in phenol) can be removed with zinc dust whereas carboxyl group (in benzoic acid) is removed by heating with soda-lime.

(*iv*) Phenol gives Liebermann's nitroso-reaction, benzoic acid does not.

(*v*) Phenol gives coupling reactions with diazonium compounds, benzoic acid does not.

(*vi*) Phenol has a typical phenolic odour, while vapours of benzoic acid are arritating in smell.

(*vii*) Phenol reacts with acetyl chloride, benzoic acid does not.

(*viii*) Benzoic acid gives esters with alcohol, phenol does not.

6. Benzoyl chloride (*Benzenecarbonyl chloride*), C_6H_5COCl

Preparation. (*i*) *It may be readily prepared by distilling benzoic acid with phosphorus pentachloride or thionyl chloride.*

$$\underset{\text{Benzoic acid}}{C_6H_5COOH} + \underset{\substack{\text{Thionyl}\\\text{chloride}}}{SOCl_2} \longrightarrow \underset{\substack{\text{Benzoyl}\\\text{chloride}}}{C_6H_5COCl} + SO_2 + HCl \quad (75\text{-}80\%)$$

(*ii*) By the action of carbonyl chloride on benzene in the presence of anhydrous $AlCl_3$ (*Friedel-Crafts Reaction*).

$$C_6H_6 + \underset{\substack{\text{Carbonyl}\\\text{chloride}}}{COCl_2} \xrightarrow{AlCl_3} \underset{\substack{\text{Benzoyl}\\\text{chloride}}}{C_6H_5COCl} + HCl$$

(*iii*) *It is manufactured by chlorinating benzaldehyde in the cold.*

$$C_6H_5CHO + Cl_2 \longrightarrow C_6H_5COCl + HCl \qquad (ex.)$$

(*iv*) Another method for the manufacture of benzoyl chloride is by heating benzoic acid with benzylidyne chloride.

$$C_6H_5COOH + C_6H_5CCl_3 \longrightarrow 2C_6H_5COCl + HCl$$

Properties. It is a colourless, fuming liquid (b. p. 470K) with a very pungent and irritating smell. Its vapours cause watering of the eyes.

(*i*) It is only very slowly decomposed by water or by dilute sodium hydroxide (*cf.*, acetyl chloride) into the free acid and hydrochloric acid.

$$C_6H_5CO\boxed{Cl + H}OH \longrightarrow C_6H_5COOH+HCl$$

(*ii*) Because of the above property, compounds containing an active hydrogen atom can be benzoylated in the presence of aqueous sodium hydroxide. *This method of benzoylation—process of replacement of active hydrogen by a benzoyl group, is known as* **Schotten-Baumann Reaction**, *e.g.*,

$$\underset{\text{Aniline}}{C_6H_5NH\,H} + Cl\,COC_6H_5 + NaOH \rightarrow \underset{\text{Benzanilide}}{C_6H_5NH.COC_6H_5} + NaCl + H_2O$$

$$\underset{\text{Phenol}}{C_6H_5O\,H} + Cl|COC_6H_5 + NaOH \rightarrow \underset{\text{Phenyl benzoate}}{C_6H_5COOC_6H_5} + NaCl + H_2O$$

$$C_6H_5CO\,\overline{Cl + H}\,OC_2H_5 + NaOH \rightarrow \underset{\text{Ethyl benzoate}}{C_6H_5COOC_2H_5} + NaCl + H_2O$$

$$C_6H_5COCl + \underset{\substack{\text{Concentrated}\\ \text{aq ammonia}}}{2NH_3} \rightarrow \underset{\text{Benzamide}}{C_6H_5CONH_2} + NH_4Cl$$

Expt Mix some aniline with excess of 10% caustic soda solution Shake it vigorously with a small excess of benzoyl chloride The insoluble benzanilide crystallizes out

(*iii*) It reacts with sodium benzoate on heating to give benzoic anhydride.

$$C_6H_5COO|\underline{Na + Cl}|CO.C_6H_5 \longrightarrow (C_6H_5CO)_2O + NaCl \qquad (g)$$

(*iv*) With benzene it reacts in the presence of anhydrous $AlCl_3$ to give benzophenone.

$$C_6H_6 + ClCOC_6H_5 \xrightarrow{AlCl_3} \underset{\text{Benzophenone}}{C_6H_5COC_6H_5} + HCl$$

(*v*) *Rosenmund's reaction* Bubbling of hydrogen through benzoyl chloride in xylene solution in presence of palladium catalyst gives benzaldehyde.

$$C_6H_5COCl + H_2 \xrightarrow{Pt} \underset{\text{Benzaldehyde}}{C_6H_5CHO} + HCl$$

Uses. Benzoyl chloride is used in benzoylation of organic compounds for identification and other purposes

7 Benzamide (*Benzenecarboxamide*), $C_6H_5CONH_2$

Preparation (*i*) *By the action of concentrated aqueous ammonia* on *benzoyl chloride*

$$C_6H_5COCl + 2NH_3 \longrightarrow C_6H_5CONH_2 + NH_4Cl \qquad (v.g.)$$

(*ii*) By hydrolysis of benzonitrile with warm alkaline hydrogen peroxide (3%)

$$C_6H_5C{\equiv}N + H_2O \xrightarrow{\text{Alk. } H_2O_2} C_6H_5CONH_2 \qquad (es.)$$

Properties. It is a white crystalline solid (m.p. 403K) insoluble in cold water but dissolves in hot water. It gives the usual reactions of an aliphatic acid amide.

For example :

(*i*) *Hydrolysis.* On boiling with dilute acid or alkali it is hydrolysed to benzoic acid.

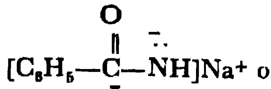
$$C_6H_5CO|\overline{NH_2 + H}|OH \longrightarrow C_6H_5COOH + NH_3$$

(*ii*) *Dehydration.* On heating with P_4O_{10} it is dehydrated to benzonitrile.

$$C_6H_5CONH_2 \xrightarrow[-H_2O]{P_4O_{10}} \underset{\text{Benzonitrile}}{C_6H_5C\equiv N}$$

(*iii*) *Formation of salts.* With mercuric oxide it forms mercury benzamide, $(C_6H_5CONH)_2Hg$.

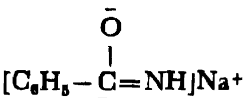
With sodium or sodamide in ethereal solution, the sodium salt $[C_6H_5CONH]^-Na^+$ is formed. Its structure may be



$$[C_6H_5-\overset{\overset{O}{\|}}{C}-\overset{-\,\cdot\cdot}{N}H]Na^+$$

I

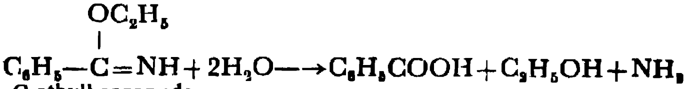
or



$$[C_6H_5-\overset{\overset{\bar{O}}{|}}{C}=NH]Na^+$$

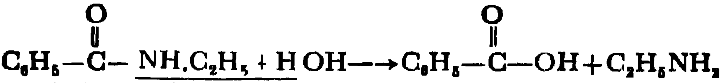
II

(*iv*) *Formation of two types of ethers.* Silver salt of benzamide reacts with ethyl iodide to give *O*-ethylbenzamide, which on hydrolysis forms benzoic acid, ethanol and ammonia.



$$\underset{O\text{-ethylbenzamide}}{C_6H_5-\overset{\overset{OC_2H_5}{|}}{C}=NH} + 2H_2O \longrightarrow C_6H_5COOH + C_2H_5OH + NH_3$$

Sodium salt on treatment with ethyl iodide gives *N*-ethylbenzamide which on hydrolysis yields benzoic acid and ethylamine.



$$\underset{N\text{-ethylbenzamide}}{C_6H_5-\overset{\overset{O}{\|}}{C}-\underline{NH.C_2H_5 + H}}\,OH \longrightarrow C_6H_5-\overset{\overset{O}{\|}}{C}-OH + C_2H_5NH_2$$

N-alkyl derivative corresponds to the formula **I** whereas *O*-alkyl derivative corresponds to the formula **II**. It is possible that **I** and **II** are resonating structures.

8. Benzoic anhydride, $(C_6H_5CO)_2O$.—It is prepared—

(*i*) *By heating sodium benzoate with benzoyl chloride.*

$$\underset{\text{Sod. benzoate}}{C_6H_5COO|\overline{Na}} + \underset{\text{Benzoyl chloride}}{\overline{Cl}|COC_6H_5} \longrightarrow \underset{\text{Benzoic anhydride}}{(C_6H_5CO)_2O} + NaCl \qquad (g.)$$

(*ii*) A better and more convenient method is *by distilling slowly a mixture of benzoic acid and acetic anhydride.*

$$2C_6H_5COOH + \underset{\text{Acetic anhydride}}{(CH_3CO)_2O} \longrightarrow \underset{\text{Benzoic anhydride}}{(C_6H_5CO)_2O} + 2CH_3COOH$$

Properties. It is a white crystalline solid (m.p. 315K). It is very slowly decomposed by water (*cf.* acetic anhydride which is more reactive). It can be used in place of benzoyl chloride in benzoylation but it is not so convenient as benzoyl chloride.

9. Benzoyl peroxide, $C_6H_5CO.O.O.COC_6H_5$.

Preparation. (*i*) *By treating benzoyl chloride with sodium peroxide*

$$2C_6H_5COCl+Na_2O_2 \longrightarrow (C_6H_5CO)_2O_2+2NaCl$$

(*ii*) *By adding benzoyl chloride and aqueous sodium hydroxide mixture to cold H_2O_2 with vigorous shaking.*

$$2C_6H_5COCl+2NaOH+H_2O_2 \longrightarrow \underset{\text{Benzoyl peroxide}}{(C_6H_5CO)_2O_2}+2NaCl+2H_2O$$

Properties. It is a colourless solid (m.p. 377K) and a fairly stable substance. It is used in free radical polymerisation processes (it readily generates the phenyl free-radical).

10. Benzonitrile (*Benzenecarbonitrile*) **C_6H_5CN.**

Preparation. (*i*) *By dehydration of benzamide with P_4O_{10}.*

$$C_6H_5CONH_2 \xrightarrow[-H_2O]{P_4O_{10}\ \text{heat}} C_6H_5CN$$

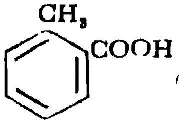
(*ii*) *From benzenediazonium chloride by means of the Sandmeyer's reaction* (*see page 2·579*).

(*iii*) *By fusing sodium benzenesulphonate with sodium cyanide* (*see page 2·527*).

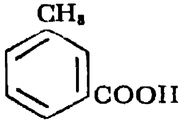
Properties. It is a colourless oil (b.p. 464K) smelling like bitter almonds. Chemically it resembles aliphatic nitriles.

HOMOLOGUES OF BENZOIC ACID

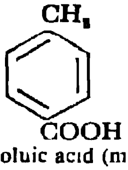
11. Toluic acids.—There are a large number of homologues of benzoic acid. We shall, however, mention only toluic acids (methylbenzoic acids) here. Three isomeric toluic acids are :



o-Toluic acid (m.p. 378K)

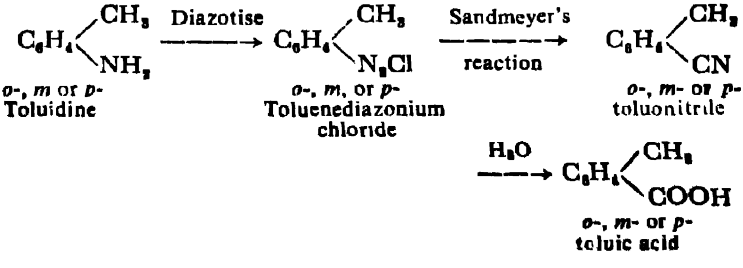


m-Toluic acid (m.p. 384K)



p-Toluic acid (m.p. 453K)

These can be prepared by oxidation of the corresponding xylenes with dilute HNO_3 or from the corresponding toluidines.

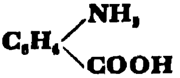


$$\underset{\text{o-, m or p-}\ \text{Toluidine}}{C_6H_4\begin{array}{l}\diagup CH_3\\ \diagdown NH_2\end{array}} \xrightarrow{\text{Diazotise}} \underset{\text{o-, m, or p-}\ \text{Toluenediazonium chloride}}{C_6H_4\begin{array}{l}\diagup CH_3\\ \diagdown N_2Cl\end{array}} \xrightarrow[\text{reaction}]{\text{Sandmeyer's}} \underset{\text{o-, m- or p-}\ \text{toluonitrile}}{C_6H_4\begin{array}{l}\diagup CH_3\\ \diagdown CN\end{array}}$$

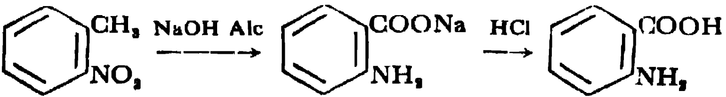
$$\xrightarrow{H_2O} \underset{\text{o-, m- or p-}\ \text{toluic acid}}{C_6H_4\begin{array}{l}\diagup CH_3\\ \diagdown COOH\end{array}}$$

Chemically toluic acids resemble benzoic acid. There is very slight difference in their acid strength (pK_a for benzoic acid=4·20 and for toluic acid=4·24). In addition there are the properties of $-CH_3$ group, an additional side-chain. For example, on oxidation it gives phthalic acid.

SUBSTITUTED BENZOIC ACIDS

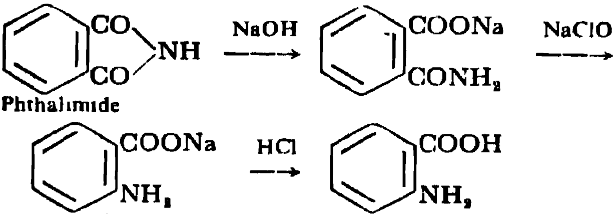
12. **Anthranilic acid**  $C_6H_4\begin{matrix}\diagup NH_2\\ \diagdown COOH\end{matrix}$ (*o-Aminobenzoic acid*).

(*i*) **Preparation.** *By reduction of o-nitrobenzoic acid or by internal oxidation of o-nitrotoluene by heating with alcoholic sodium hydroxide.*



o-Nitrotoluene Anthranilic acid

(*ii*) **Manufacture.** *By oxidation of phthalimide with aqueous sodium hydroxide and sodium hypochlorite (Hofmann reaction).*



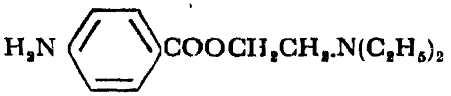
Phthalimide

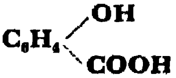
Sod. anthranilate Anthranilic acid

Properties and Uses It is a white solid (m.p. 418K), sweet in taste and soluble in water, alcohol and ether. On heating it loses CO_2 and forms aniline. It gives usual reactions of an amine and an acid

It is used in the manufacture of indigotin. Methyl anthranilate is used in perfumery Characteristic smell of jasmine and orange blossoms is due to the presence of methyl anthranilate.

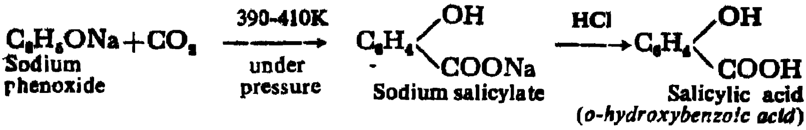
13 ***p*-Aminobenzoic acid.** It may be prepared by reducing *p*-nitrobenzoic acid *p*-Aminobenzoic acid (m.p. 459K) is one of the substances constituting vitamin B complex. Certain derivatives of it are local anaesthetics, *e.g.*, novocaine.



14. **Salicylic acid (*o*-hydroxybenzoic acid),**  $C_6H_4\begin{matrix}\diagup OH\\ \diagdown COOH\end{matrix}$

There are three hydroxybenzoic acids—the *o*-, *m*- and *p*- isomers. Out of these only the *o*-isomer (salicylic acid) is important It occurs as methyl salicylate in many essential oils.

Preparation. (*i*) *By heating solid sodium phenoxide to 390-410K with carbon dioxide under pressure*—**Kolbe's Reaction.**



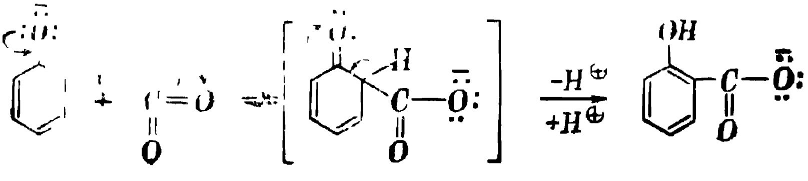
$$\underset{\text{Sodium phenoxide}}{C_6H_5ONa+CO_2} \xrightarrow[\text{under pressure}]{390\text{-}410K} \underset{\text{Sodium salicylate}}{C_6H_4\left\langle\begin{matrix}OH\\COONa\end{matrix}\right.} \xrightarrow{HCl} \underset{\text{Salicylic acid}}{C_6H_4\left\langle\begin{matrix}OH\\COOH\end{matrix}\right.}$$

(*o-hydroxybenzoic acid*)

In fact this method is a modification of the original Kolbe's reaction and is known as **Kolbe-Schmitt method.**

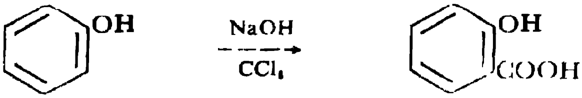
A small amount of *p*-isomer is also obtained along with the *o*-isomer. If, however, the temperature rises above 415K, the *p*-isomer is the main product. Similarly, if potassium phenoxide is taken instead of sodium phenoxide, the *p*-isomer is the main product.

The probable mechanism of this reaction is the attack on the activated carbon atom of the ring by the weakly electrophilic CO_2.



Salicylate anion

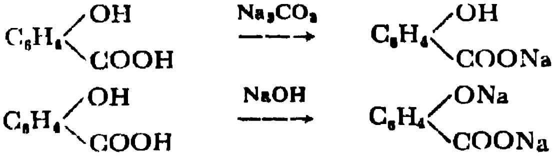
(*ii*) *By heating phenol with carbon tetrachloride and alcoholic potash* (**Reimer-Tiemann Reaction**). (*cf.* page 2·607).



Properties : Physical. Salicylic acid gives colourless needle-shaped crystals (m.p. 429K), sparingly soluble in cold water but readily soluble in hot water, alcohol, ether and chloroform. It sublimes on heating quickly below its melting point and is volatile in steam. It is poisonous in nature and possesses antiseptic properties.

Chemical. Due to the presence of a carboxyl and a phenolic group, salicylic acid combines in it the properties of an acid and a phenol.

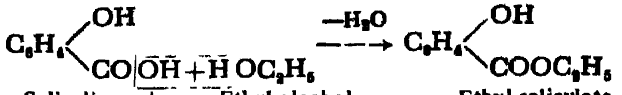
(*i*) A metal carbonate reacts with the carboxyl group while an alkali reacts with both phenolic and carboxyl groups to give dimetallic derivatives.



$$C_6H_4\left\langle\begin{matrix}OH\\COOH\end{matrix}\right. \xrightarrow{Na_2CO_3} C_6H_4\left\langle\begin{matrix}OH\\COONa\end{matrix}\right.$$

$$C_6H_4\left\langle\begin{matrix}OH\\COOH\end{matrix}\right. \xrightarrow{NaOH} C_6H_4\left\langle\begin{matrix}ONa\\COONa\end{matrix}\right.$$

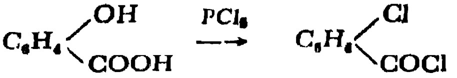
(*ii*) With alcohols in the presence of gaseous hydrogen chloride, the carboxyl group is reacted forming esters.



$$C_6H_4\begin{cases}OH\\ CO|\overline{OH+H}\,OC_2H_5\end{cases}\xrightarrow{-H_2O} C_6H_4\begin{cases}OH\\ COOC_2H_5\end{cases}$$

Salicylic acid Ethyl alcohol Ethyl salicylate

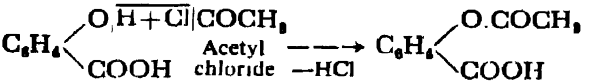
(*iii*) With phosphorus pentachloride, both the groups are reacted.



$$C_6H_4\begin{cases}OH\\ COOH\end{cases}\xrightarrow{PCl_5} C_6H_4\begin{cases}Cl\\ COCl\end{cases}$$

Salicylic acid *o*-chlorobenzoyl chloride

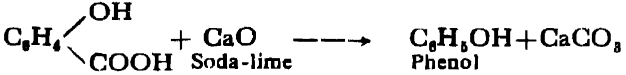
(*iv*) With acid chlorides and anhydrides the phenolic group is acylated.



$$C_6H_4\begin{cases}O\overline{H+Cl}|COCH_3\\ COOH\end{cases}\underset{\text{chloride}}{\text{Acetyl}}\xrightarrow[-HCl]{} C_6H_4\begin{cases}O.COCH_3\\ COOH\end{cases}$$

Salicylic acid Acetylsalicylic acid (*Aspirin*)

(*v*) When heated with soda-lime the —COOH group is removed yielding phenol.

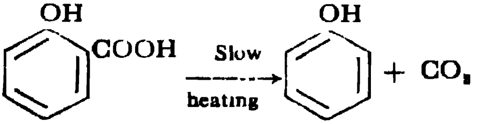


$$C_6H_4\begin{cases}OH\\ COOH\end{cases}+\underset{\text{Soda-lime}}{CaO}\longrightarrow \underset{\text{Phenol}}{C_6H_5OH}+CaCO_3$$

Salicylic acid

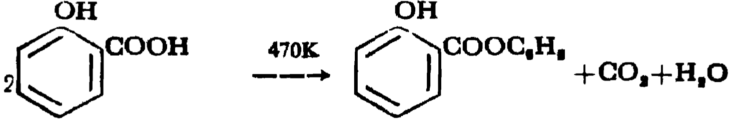
(*vi*) With ferric chloride (neutral solution) it gives violet colour (*property of the phenolic group*).

(*vii*) When heated slowly, it undergoes decarboxylation to yield phenol.



The ease of decarboxylation increases as the number of OH groups in *o*- and *p*-positions with respect to carboxyl group increases in a molecule.

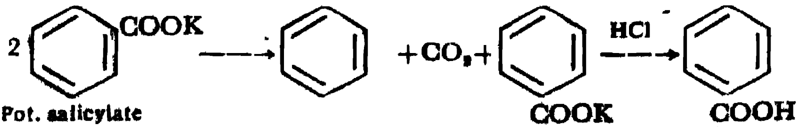
On heating to above 470K, it gives phenyl salicylate.



Salicylic acid Phenyl salicylate

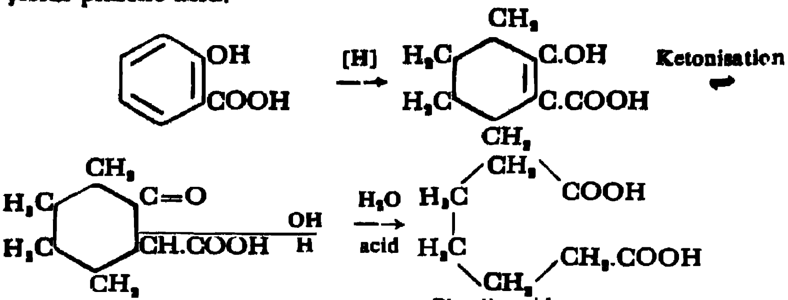
Probably phenol obtained by decarboxylation of salicylic acid combines with one molecule of the acid to give phenyl salicylate.

(*viii*) On heating potassium salicylate at 400K, *p*-hydroxybenzoic acid is obtained.



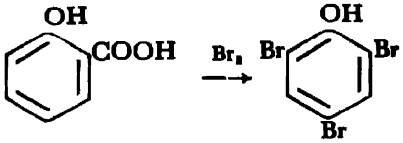
Pot. salicylate *p*-Hydroxybenzoic acid

(*ix*) ***Reduction.*** **On reduction with sodium and isopentanol, it yields pimelic acid.**



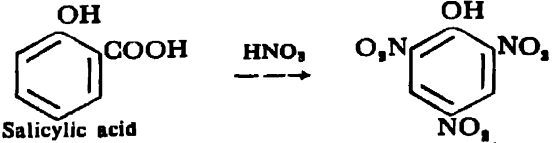
Pimelic acid

(*x*) ***Bromination.*** On treatment with bromine water, salicylic acid gives *s*-tribromophenol. Here the —COOH is also replaced by a bromine atom. This is a characteristic property of the —COOH group when present in position *o*- or *p*- to a hydroxyl or amino group.



s-tribromophenol

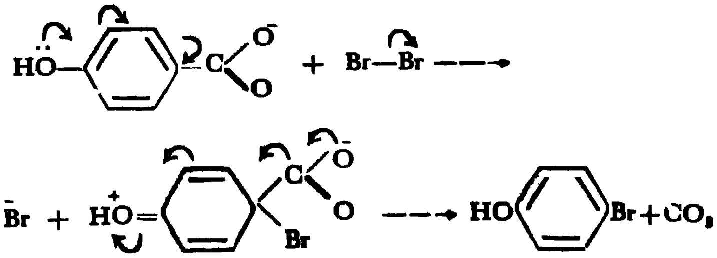
(*xi*) *Nitration*. As in bromination, the —COOH group is replaced by a —NO_2 group on nitration and *s*-trinitrophenol is produced.



Salicylic acid

s-trinitrophenol

The reason for this ready displacement of the carboxyl group by bromine or nitro group is not certain, but the mechanism involved is possibly as under :



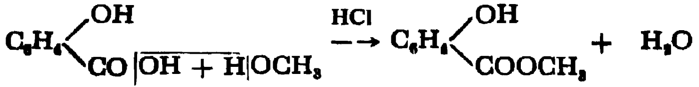
Uses. (*i*) **As an antiseptic.**

(*ii*) **As medicine for rheumatic pain.**

(*iii*) For the manufacture of methyl salicylate (used in perfumery), aspirin and salol.

(*iv*) In the preparation of azo-dyes.

15. **Methyl salicylate** (*o*-**HO.C_6H_4.$COOCH_3$**).—It is the principal constituent of oil of wintergreen and may be prepared by direct esterification—by distilling salicylic acid with methanol in the presence of hydrogen chloride.

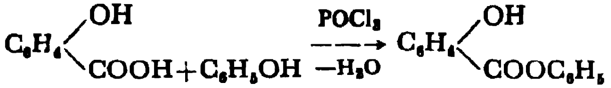


$$C_6H_4\left<\begin{matrix}OH\\ CO\,|\overline{OH + H}|OCH_3\end{matrix}\right. \xrightarrow{HCl} C_6H_4\left<\begin{matrix}OH\\ COOCH_3\end{matrix}\right. + H_2O$$

Salicylic acid　　　Methyl salicylate

It is a colourless, pleasant-smelling liquid (b.p. 295K) used in perfumery and as a flavouring material. It is also used in medicine : in rheumatism and as a remedy for sprains and bruises.

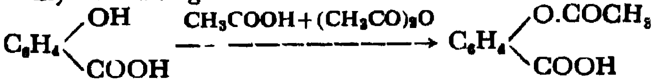
16. **Salol (phenyl salicylate)**, *o*-**$HOC_6H_4COOC_6H_5$**.—It is prepared by heating salicylic acid with phenol in the presence of phosphoryl chloride.



$$C_6H_4\left<\begin{matrix}OH\\ COOH\end{matrix}\right. + C_6H_5OH \xrightarrow[-H_2O]{POCl_3} C_6H_4\left<\begin{matrix}OH\\ COOC_6H_5\end{matrix}\right.$$

It is a white solid (m.p 316K) used as an internal antiseptic

17. **Aspirin**, *o*-**$CH_3CO.O.C_6H_4$ COOH (acetylsalicylic acid)**.—It is prepared by acetylating salicylic acid with a mixture of acetic anhydride and glacial acetic acid.



$$C_6H_4\left<\begin{matrix}OH\\ COOH\end{matrix}\right. \xrightarrow{CH_3COOH+(CH_3CO)_2O} C_6H_4\left<\begin{matrix}O.COCH_3\\ COOH\end{matrix}\right.$$

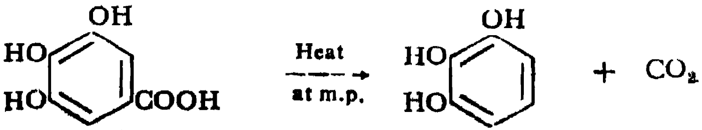
Salicylic acid　　　Aspirin

It is a white solid (m.p. 408K) used for relieving pain.

18. **Gallic acid** (*3 : 4 : 5-Trihydroxybenzoic acid*), **$C_6H_2(OH)_3$. COOH**.—Gallic acid occurs in tea and many plants, *e.g* , gall nuts, oak bark, acacia bark. Tannin (tannic acid) is a complex glucoside of gallic acid. Gallic acid is prepared by boiling tannin with dilute acids and extracting the gallic acid set free with ether.

Properties. It forms white needle-shaped crystals (m.p. 530K) which readily dissolve in hot water, ethanol and ether.

(*i*) *Action of heat.* It is decarboxylated when heated at its melting point and yields 1, 2, 3-benzenetriol.



Gallic acid　　　1, 2, 3-Benzenetriol

(*ii*) ***Reducing agent.*** It is a powerful reducing agent and on this account used as photographic developer. It reduces ammoniacal silver nitrate solution.

(*iii*) *Absorbs oxygen.* An alkaline solution of gallic acid absorbs oxygen from air and turns brown.

(*iv*) *With ferric chloride.* An aqueous solution of gallic acid gives a blue-black precipitate with ferric chloride. On account of this property gallic acid is used in making blue-black ink.

Uses. (*i*) It is used in the manufacture of dyes.

(*ii*) In preparing blue-black ink.

(*iii*) As photographic developer.

(*iv*) In making 1, 2, 3-Benzenetriol

19. **Blue-Black Ink.**—Various ingredients of blue-black ink are:

Gallic acid	
Ferrous sulphate	
Blue dye	
Gums, etc.	...Protective agent
Phenol (in traces)	...Preservative
Sulphuric acid (a little)	...To retard oxidation.

When we write with this ink on paper, the sulphuric acid present in the ink is neutralised by ammonia of the paper. In the absence of sulphuric acid ferrous sulphate is readily oxidised to ferric sulphate which gives an intensely black precipitate with gallic acid. In this way writing becomes intensely black on drying.

20. **The ortho-effect.**—It has been found that the properties of ortho compounds usually differ from those of the corresponding meta- and para-isomers. For example,

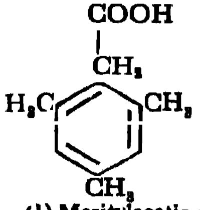
(*i*) Aminopentamethylbenzene gives little or no quaternary ammonium compound when heated with methyl iodide.

(*ii*) Benzaldehyde reacts with aniline to form an anil but not with *s*-tribromoaniline.

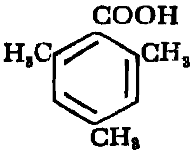
(*iii*) Benzoic acid and *o*-substituted benzoic acid form methyl esters with methanol and hydrogen chloride but under the same conditions di- ortho-substituted benzoic acid fail to form methyl esters.

Victor Meyer (1894) explained these abnormal observations as due to **steric hindrance.** According to him groups present in the ortho-position mechanically interfered in the reactions of $-NH_2$, $-CHO$ or $-COOH$ group tending to shield it from the attacking reagent.

It has been observed that mesitylacetic acid (I) undergoes esterification readily but mesitoic acid (II) does not at all undergo esterification



(I) Mesitylacetic acid



(II) Mesitoic acid

This is explained by saying that —COOH group in mesitylacetic acid being away from the ring is not shielded by $—CH_3$ groups in the ortho-positions as in mesitoic acid.

As a result of his experiments on esterification of substituted benzoic acids, Kellas (1897) found that—

(*i*) Rates of esterification were in the order :

m-isomer > *p*-isomer > *o*-isomer.

On the basis of steric hindrance (a purely spatial effect), rates of esterification of *m*- and *p*-isomers should have been the same.

(*ii*) Presence of nitro group hindered esterification more than the presence of iodine atom. Nitro group being smaller in size than iodine atom should interfere less in terms of steric hindrance.

At present it is felt that such abnormalities cannot be explained by mechanical interference alone. In addition to the spatial factor, the polar influence of the substituents and other factors (chelation and steric inhibition of resonance) play a prominent part in these reactions.

The term steric hindrance to denote a spatial effect is, therefore, misleading. Chemists prefer to term it as the **proximity effect**. The **ortho-effect** is a special case of the proximity effect being used only in the case of nuclear substituents. The term steric hindrance is, however, still being used to denote the proximity effect.

MONOBASIC ACIDS WITH THE CARBOXYL GROUP IN THE SIDE-CHAIN

21. **Phenylacetic acid** (*α-Toluic acid*), $C_6H_5CH_2COOH$.—It is a typical acid with carboxyl group in the side-chain and is isomeric with toluic acids. It occurs in certain esters.

Preparation. (*i*) *From benzyl chloride.*

$$\underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} \xrightarrow{KCN} \underset{\text{Phenylacetonitrile}}{C_6H_5CH_2CN} \xrightarrow[H_2SO_4]{H_2O} \underset{\text{Phenylacetic acid}}{C_6H_5CH_2COOH}$$

(*ii*) *By reducing mandelonitrile with hydriodic acid and red phosphorus.*

$$\underset{\text{Mendelonitrile}}{C_6H_5CH(OH)CN} \xrightarrow{\text{HI/red P}} C_6H_5CH_2COOH$$

Properties. It is a white crystalline solid (m.p. 350K) having an unpleasant smell. It is soluble in hot water. Due to the presence of two α-hydrogen atoms, it is reactive both in the side-chain as well as in the nucleus. For example,

(*i*) On chlorination in the cold and in the presence of halogen carrier substitution occurs in the nucleus and *o*- and *p*-substitution products are obtained.

(*ii*) On chlorination at the boiling point and in the absence of halogen carrier side-chain substitution products are obtained by replacement of α-hydrogen atoms (*cf.* chlorination of toluene, page 2·483).

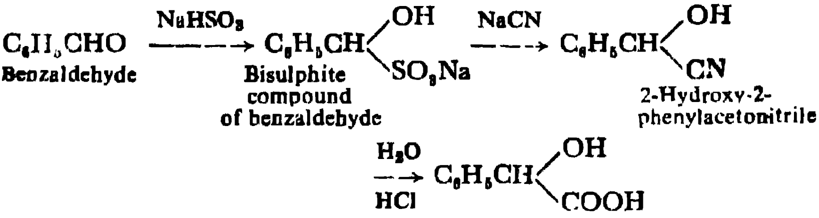
(*iii*) It is a stronger acid as compared with acetic acid. This is due to electron withdrawing character of phenyl group.

(*iv*) On oxidation with chromic acid it gives benzoic acid. Isomeric toluic acids are oxidised to phthalic acids.

22. Mandelic acid $C_6H_5CHOH.COOH$. (*Phenylglycollic acid*).—Amygdalin present in bitter almonds is a glucoside of myndelic acid.

Preparation. (*i*) *By regulated hydrolysis of amygdalin.* (*See* page 2·627).

(*ii*) *By adding a saturated $NaHSO_3$ solution to a mixture of benzaldehyde and aqueous sodium cyanide.*



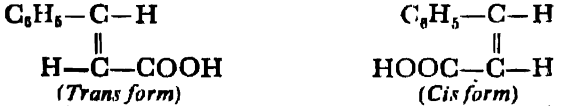
$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} \xrightarrow{NaHSO_3} \underset{\text{Bisulphite compound of benzaldehyde}}{C_6H_5CH\begin{smallmatrix}OH\\SO_3Na\end{smallmatrix}} \xrightarrow{NaCN} \underset{\text{2-Hydroxy-2-phenylacetonitrile}}{C_6H_5CH\begin{smallmatrix}OH\\CN\end{smallmatrix}}$$

$$\xrightarrow[HCl]{H_2O} C_6H_5CH\begin{smallmatrix}OH\\COOH\end{smallmatrix}$$

Mandelic acid

Properties. It is a white crystalline solid moderately soluble in water. It is optically active and behaves as a hydroxy-acid. The acid (m p. 406K) is obtained from amygdalin. Synthetically prepared acid is (±)-variety (m.p. 291K). It forms benzoic acid on vigorous oxidation. While on reduction with hydriodic acid, it gives phenylacetic acid. Mandelic acid finds use as an internal antiseptic.

23 Cinnamic acid $C_6H_5CH{=}CH.COOH$, (*β-Phenylacrylic acid*).—Due to the presence of a double bond it exhibits geometrical isomerism. The two forms are :



$$\begin{matrix}C_6H_5-C-H\\ \|\\ H-C-COOH\end{matrix} \qquad \begin{matrix}C_6H_5-C-H\\ \|\\ HOOC-C-H\end{matrix}$$

(*Trans form*) Cinnamic acid)

(*Cis form*) Allocinnamic acid

The trans variety is termed *cinnamic acid* and is the form which occurs in nature free and as esters in balsams and resins. The cis variety is called *allocinnamic acid.*

Preparation. Cinnamic acid may be prepared :

(*i*) *By heating benzaldehyde with acetic anhydride in presence of sodium acetate* (*Perkin's reaction*).

$$C_6H_5CH{=}O+(CH_3CO)_2O \xrightarrow{CH_3COONa} C_6H_5CH{=}CH.COOH$$

(*ii*) *By the action of malonic acid in ethanolic ammonia on benzaldehyde in presence of pyridine* (*Knoevenagel reaction*)

$$C_6H_5CH{=}O+CH_2(COOH)_2 \xrightarrow[\text{heat}]{NH_3/C_2H_5OH} \underset{\text{Cinnamic acid}}{C_6H_5CH{=}CH.COOH}$$

(*iii*) ***By condensation of benzdalehyde and ethyl acetate in presence of sodium ethoxide*** (*Claisen condensation*).

$$C_6H_5CH{=}O + CH_3COOC_2H_5 \xrightarrow{C_2H_5ONa} C_6H_5.CH{=}CH.COOC_2H_5$$

$$\xrightarrow[\text{acid}]{H_2O} C_6H_5CH{=}CH.COOH + C_2H_5OH$$

Manufacture. It is, however, manufactured :

(*i*) ***By heating benzylidene chloride with sodium acetate followed by acidification.***

$$C_6H_5CH\,\overline{Cl_2 + H_2}|CH.COONa \xrightarrow[-2HCl]{\text{Heat}}$$

$$\underset{\text{Sod. cinnamate}}{C_6H_5CH{=}CHCOONa} \xrightarrow{\text{Acidify}} \underset{\text{Cinnamic acid}}{C_6H_5CH{=}CH.COOH}$$

(*ii*) ***By oxidising benzylideneacetone with alkaline sodium hypochlorite*** (*cf.* Haloform reaction in which acetone gives sodium acetate).

$$\underset{\text{Benzylideneacetone}}{C_6H_5CH{=}CH.COCH_3} \xrightarrow[\text{Oxidation}]{NaClO} \underset{\text{Cinnamic acid}}{C_6H_5CH{=}CHCOOH}$$

Properties. It is a white crystalline solid (m.p. 406K) with a sharp odour. It is very slightly soluble in water. Its reactions are those of an αβ-unsaturated acid and of the benzene nucleus. For example :

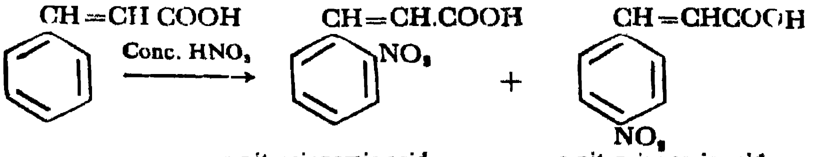
(*i*) *Reduction* On reduction with sodium amalgam and water it gives β-Phenylpropionic acid.

$$C_6H_5CH{=}CH.COOH \xrightarrow[H_2O]{Na/Hg} \underset{\beta\text{-Phenylpropionic acid}}{C_6H_5CH_2.CH_2.COOH}$$

(*ii*) *Oxidation.* On oxidation with chromic acid, it gives a mixture of benzaldehyde and benzoic acid.

$$C_6H_5CH{=}CH\,COOH \xrightarrow{[O]} \underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

(*iii*) *Nitration.* With concentrated nitric acid it undergoes nitration to give *o*- and *p*-nitrocinnamic acids. The *p*-isomer predominates in the mixture.

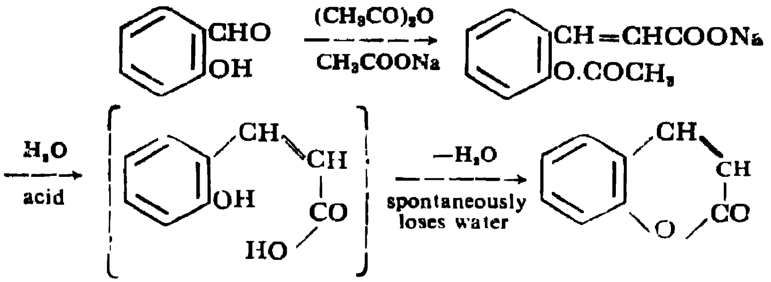


o-nitrocinnamic acid *p*-nitrocinnamic acid

(*iv*) *Decarboxylation.* When heated for some time just above its melting point or when distilled with soda-lime it forms styrene.

$$\underset{\text{Sod. cinnamate}}{C_6H_5.CH{=}CH|\overline{COONa + NaO}|H} \longrightarrow \underset{\text{Styrene}}{C_6H_5CH{=}CH_2} + Na_2CO$$

24. Coumarin.—It may be obtained from salicylaldehyde by Perkin's reaction.



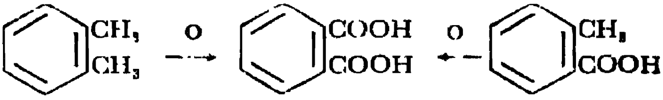
Coumarinic acid
(*o- hydroxyallocinnamic acid*)
(*Unstable*)

Coumarin
(γ-lactone of
coumarinic acid)

It is a white crystalline solid (m.p. 340K). It is a natural perfume and is used as an artificial flavour. It changes into coumaric acid (*o-hydroxycinnamic acid*), when heated with sodium ethoxide.

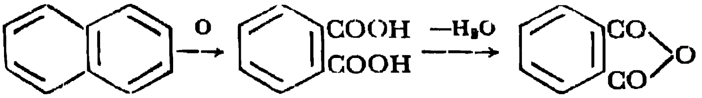
25. Phthalic acid (1, 2-Benzenedicarboxylic acid), $C_6H_4(COOH)_2$.

Preparation. (*i*) *In the laboratory*, phthalic acid may be prepared by the oxidation of *o*-xylene or *o*-toluic acid. Dilute nitric acid or permanganate is used as the oxidising agent. Chromic acid cannot be used as with it the ring gets ruptured.

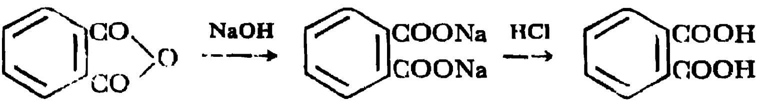


o-Xylene Phthalic acid *o*-Toluic acid

(*ii*) *In commerce*, phthalic acid was formerly prepared by the oxidation of naphthalene ($C_{10}H_8$) with fuming sulphuric acid at 570K in presence of a little mercury or mercuric sulphate (*catalyst*). This method is almost obsolete today. It is now manufactured by passing vapours of naphthalene with excess of air over heated vanadium pentoxide (670K). The anhydride that distils over is boiled with alkali and then acidified to get free acid. Some maleic acid is also obtained as a by-product.



Naphthalene Phthalic acid Phthalic anhydride

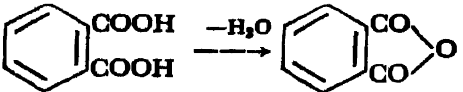


Recent method for the manufacture of phthalic acid is by catalytic oxidation of *o*-xylene obtained from petroleum.

Properties : Physical. It is a colourless crystalline substance (m.p. 457K) soluble in water and organic solvents.

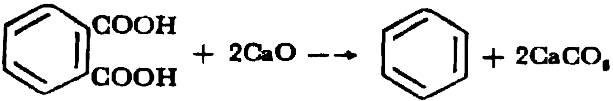
Chemical. Phthalic acid is a dibasic acid and gives the usual reactions of two —COOH groups.

(*i*) **Action of Heat.** On heating it loses water to give phthalic anhydride (m. p. 504K).



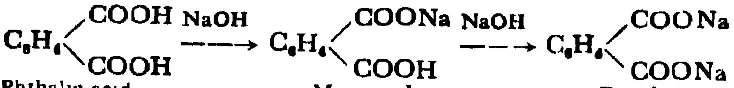
Phthalic acid Phthalic anhydride

(*ii*) **Heating with Soda-lime.** On heating with soda-lime, it gives benzene.



Phthalic acid Benzene

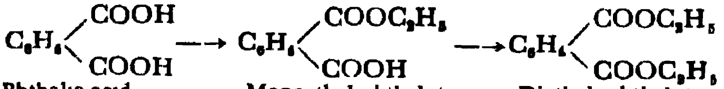
(*iii*) **Neutralization.** With alkalis, *e.g.*, sodium hydroxide, it forms two series of salts—mono and disodium salts.



$$C_6H_4\begin{cases}COOH\\COOH\end{cases}\xrightarrow{NaOH}C_6H_4\begin{cases}COONa\\COOH\end{cases}\xrightarrow{NaOH}C_6H_4\begin{cases}COONa\\COONa\end{cases}$$

Phthalic acid Mono-sodium phthalate Disodium phthalate

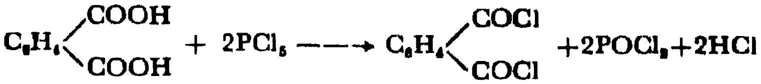
(*iv*) **Esterification.** With alcohols it gives two series of esters — acid and normal esters.



$$C_6H_4\begin{cases}COOH\\COOH\end{cases}\longrightarrow C_6H_4\begin{cases}COOC_2H_5\\COOH\end{cases}\longrightarrow C_6H_4\begin{cases}COOC_2H_5\\COOC_2H_5\end{cases}$$

Phthalic acid Monoethyl phthalate Diethyl phthalate (*normal ester*)

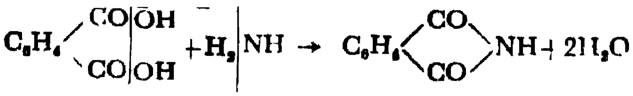
(*v*) **With Phosphorus Pentachloride** it gives the acid chloride (phthaloyl chloride).



$$C_6H_4\begin{cases}COOH\\COOH\end{cases}+2PCl_5\longrightarrow C_6H_4\begin{cases}COCl\\COCl\end{cases}+2POCl_3+2HCl$$

Phthaloyl chloride or phthalyl chloride

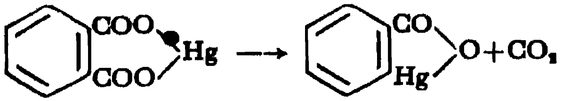
(*vi*) **Heat with Ammonia** When heated with ammonia it gives phthalimide.



$$C_6H_4\begin{cases}CO\,OH\\CO\,OH\end{cases}+H_2\,NH\rightarrow C_6H_4\begin{cases}CO\\CO\end{cases}NH+2H_2O$$

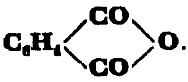
(*vii*) **Reduction** On reduction with sodium amalgam it gives di-, tetra- and hexahydrophthalic acids.

(viii) Mercuration. Phthalic acid is mercurated by fusing it with mercuric acetate or mercuric phthalate till mercuration occurs.



Uses. In the manufacture of plastics, dyes, *e.g.*, indigo, cosine, fluorescein and other compounds.

26. Phthalic anhydride,

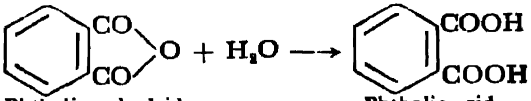


$$C_6H_4\langle{}^{CO}_{CO}\rangle O.$$

Preparation. It is prepared industrially by the oxidation of naphthalene or *o*-xylene as given above.

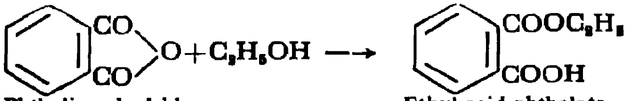
Properties. It is a white solid (m.p. 401K) almost insoluble in cold water.

(*i*) *Hydrolysis.* It is slowly hydrolysed by hot water but rapidly by alkalis or acids.



Phthalic anhydride Phthalic acid

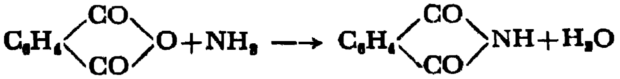
(*ii*) *Esterification.* With alcohols and glycols it gives half esters.



Phthalic anhydride Ethyl acid phthalate

With excess of alcohol in presence of sulphuric acid half esters can be converted into normal esters.

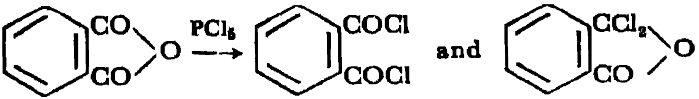
(*iii*) When heated with dry ammonia under pressure at about 470K, phthalimide is obtained.



$$C_6H_4\langle{}^{CO}_{CO}\rangle O+NH_3 \longrightarrow C_6H_4\langle{}^{CO}_{CO}\rangle NH+H_2O \quad (90\%)$$

Phthalic anhydride Phthalimide

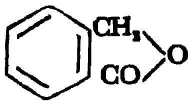
(*iv*) *Formation of acid chloride.* Phthalic anhydride reacts with PCl_5 to give phthaloyl chloride which exists in two forms I and II.



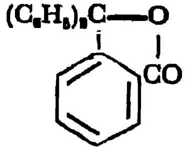
I-Symmetrical *II-Unsymmetrical*

Two forms of phthaloyl or phthalyl chloride.

The symmetrical form changes into the unsymmetrical form when heated with $AlCl_3$. Derivatives of both of them are known but those of II are most important and very interesting. Two of these are phthalide and phthalophenone.

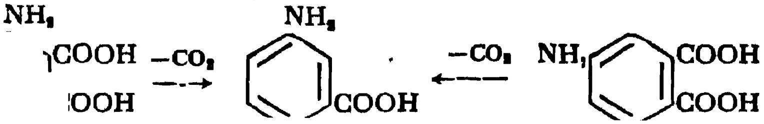


Phthalide



Phthalophenone

(*v*) On nitration, it gives a mixture of 3- and 4-nitrophthalic acids. These on reduction give the corresponding aminophthalic acids which lose CO_2 to yield *m*-aminobenzoic acid.



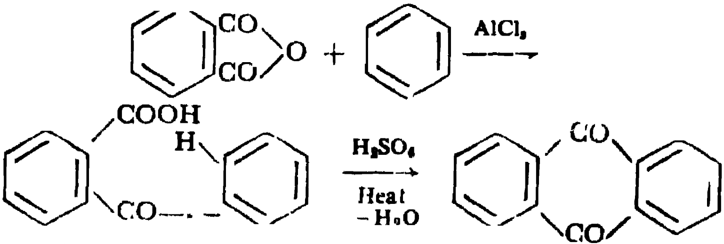
3-Amino-phthalic acid

m-Amino-benzoic acid

4-Amino-phthalic acid

Here we find that in either case —COOH group *o*- or *p*- to the $-NH_2$ group is lost.

(*vi*) *Condensation with aromatic hydrocarbons.* It is a typical Friedel-Crafts reaction. It condenses with benzene in the presence of $AlCl_3$ to give anthraquinone.



o-Benzoylbenzoic acid

Anthraquinone

(*vii*) *Condensation with phenols.* When heated with phenol and a drop of concentrated sulphuric acid, phthalic anhydride gives phenolphthalein (*see* page 2·609).

Similarly with 1, 3-benzenediol it condenses to give fluorescein.

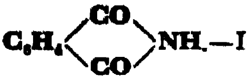
Uses. Phthalic anhydride is used in the manufacture of—

(*i*) Alkyl phthalates used as plasticizers. Dimethyl phthalate (DMP) is an insect repellant.

(*ii*) Polyester resins, *e.g.*, *glyptal* (from glycerol and phthalic anhydride).

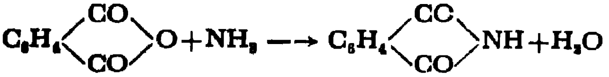
(*iii*) Anthraquinone and its derivatives which are used in the synthesis of dyes.

(*iv*) Miscellaneous compounds like benzoic acid, phthalimide, phenolphthalein, fluorescein, etc.



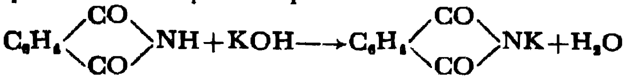
$$C_6H_4\langle{}^{CO}_{CO}\rangle NH$$

27. Phthalimide, $C_6H_4(CO)_2NH$.—It may be obtained by heating phthalic anhydride with dry ammonia under pressure at about 470K.



$$C_6H_4\langle{}^{CO}_{CO}\rangle O+NH_3 \longrightarrow C_6H_4\langle{}^{CO}_{CO}\rangle NH+H_2O \qquad (90\%)$$

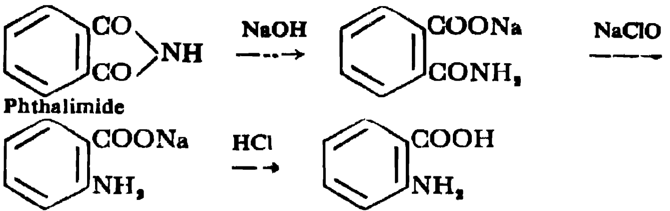
It is a white solid, weakly acidic in character, *e.g.*, with alcoholic potash it forms potassio-phthalimide.



$$C_6H_4\langle{}^{CO}_{CO}\rangle NH+KOH \longrightarrow C_6H_4\langle{}^{CO}_{CO}\rangle NK+H_2O \qquad (68\%)$$

If forms phthalic acid when hydrolysed with warm aqueous alkali.

On oxidation with alkaline sodium hypochlorite, phthalimide gives anthranilic acid.



Phthalimide

Anthranilic acid

It is used in Gabriel's synthesis of primary amines and in the preparation of an anthranilic acid, etc.

28. Acidity of Aromatic Acids.—An aromatic acid ArCOOH ionizes as follows :

$$ArCOOH + H_2O \rightleftharpoons ArCOO^- + H_3O^+$$

The equilibrium constant for the system is termed ionization constant, K_a of the acid and is a measure of its acidity.

$$K_a = \frac{[ArCOO^-]\,[H_3O^+]}{[ArCOOH]}$$

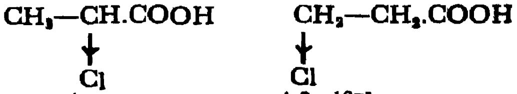
Water being present in large excess, $[H_2O]$ remains constant and is omitted. K_a values of some acids are given below. These will help us to know the relative acidity of various acids.

Table 44·1—Comparison of Acidities of some aromatic acids

Acid	K_a at 298K	Acid	K_a at 298K
Benzoic acid	$6{\cdot}46\times10^{-5}$	*p*-Nitrobenzoic acid	$3{\cdot}9\times10^{-4}$
p-Toluic acid	$4{\cdot}33\times10^{-5}$	*m*-Nitrobenzoic acid	$3{\cdot}2\times10^{-4}$
m-Toluic acid	$5{\cdot}4\times10^{-5}$	*o*-Nitrobenzoic acid	$6{\cdot}7\times10^{-4}$
o-Toluic acid	$12{\cdot}4\times10^{-5}$	*p*-Hydroxybenzoic acid	$2{\cdot}6\times10^{-4}$
p-Chlorobenzoic acid	$10{\cdot}4\times10^{-5}$	*m*-Hydroxybenzoic acid	$8{\cdot}3\times10^{-4}$
m-Chlorobenzoic acid	$15{\cdot}1\times10^{-5}$	*o*-Hydroxybenzoic acid	$10{\cdot}5\times10^{-4}$
o-Chlorobenzoic acid	$10{\cdot}2\times10^{-4}$		

Effect of Substituents on Acidity. As discussed on page 2·229, an electron-withdrawing substituent increases the acidity of a carboxylic acid and an electron-releasing substituent decreases it.

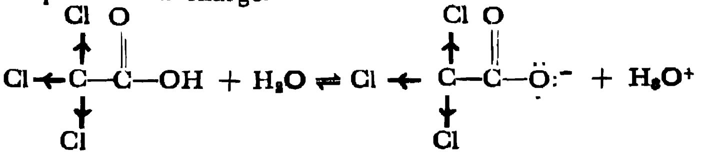
In aliphatic acids the acid-strengthening effect of electron-withdrawing substituents is primarily due to their inductive effect which decreases as the distance of the substituent from the carboxyl group increases. For example, α-chloropropionic acid is stronger than β-chloropropionic acid



$$CH_3-\underset{\underset{Cl}{\downarrow}}{C}H.COOH \qquad \underset{\underset{Cl}{\downarrow}}{C}H_2-CH_2.COOH$$

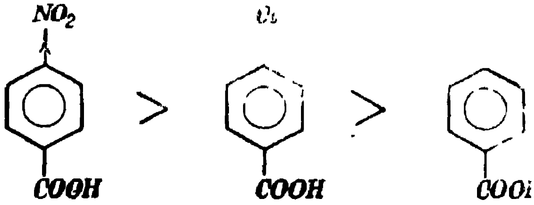
K_a : $1{\cdot}47\times10^{-3}$ $\qquad$ $1{\cdot}3\times10^{-4}$

Electron-withdrawing groups increase the acidity of aliphatic acids since these stabilise the negatively charged carboxylate ion by dispersal of its charge.



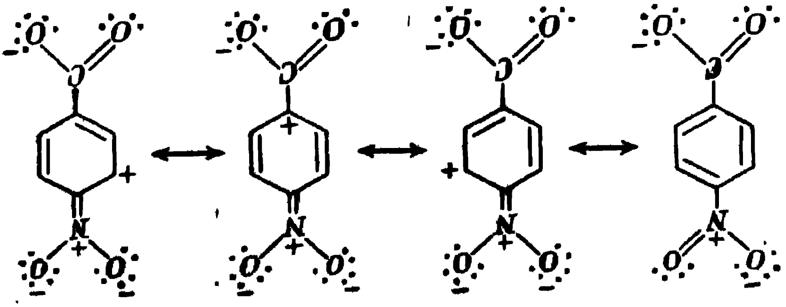
Carboxylate ion stabilised by dispersal of charge

Similarly electron-withdrawing substituents increase the acidity of aromatic acids also. For example, both *p*-nitrobenzoic acid and *p*-chlorobenzoic acid are stronger than benzoic acid.



K_a : $3{\cdot}93\times10^{-4}$ $\qquad$ $1{\cdot}04\times10^{-4}$ $\qquad$ $6{\cdot}46\times10^{-5}$

p-nitrobenzoic acid is stronger than *p*-chlorobenzoic acid because with *p*-nitro group, inductive as well as resonance effects are important in stabilizing the carboxylate ion.



Resonance structures for the *p*-nitrobenzoate ion

Thus we find that while considering the effect of substituents on aromatic carboxylic acids, we must take into account their inductive as well as resonance effects. In *p*-nitrobenzoic acid the nitro group exerts electron-withdrawing inductive effect as well as electron-withdrawing resonance effect.

From Table 44·1, we learn that *p*-nitrobenzoic acid ($K_a = 3 \cdot 9 \times 10^{-4}$) is stronger than *m*-nitrobenzoic acid ($K_a = 3 \cdot 2 \times 10^{-4}$). This is because by resonance effect the nitro group withdraws electrons from *ortho-para* positions and not from *meta* position. Thus in the case of *m*-nitrobenzoic acid increase in acidity is only due to electron-withdrawing inductive effect of nitro group. It is, therefore, a weaker acid compared to *p*-nitrobenzoic acid.

To summarise, *the nitro group exerts greater electron-withdrawing effect when present in ortho-para positions.* This explains why *o*- and *p*-nitrobenzoic acid are stronger than *m*-nitrobenzoic acid which is, of course, stronger than benzoic acid.

In the case of hydroxybenzoic acids, the OH group exerts an electron-withdrawing inductive effect and, therefore, tends to decrease the electron density at all positions.

However, due to its resonance effects it tends to increase the electron density at ortho and para positions while the meta position remains almost unaffected. Thus we find there is decrease in electron density at all positions due to inductive effect but increase in electron density at ortho and para positions due to resonance effect. The resonance effect being stronger as compared to inductive effect there is net increase in electron density at ortho and para positions. *p*-Hydroxybenzoic acids is, therefore, weaker than benzoic acid.

There is net decrease in electron density at meta position due to electron-withdrawing inductive effect of OH group. *m*-Hydroxybenzoic acid is, therefore, stronger than benzoic acid.

Based on the explanation given above *o*-hydroxybenzoic acid should be weaker than benzoic acid but is actually the strongest among benzoic acid and three hydroxybenzoic acids. Further practically all groups when present in ortho position to COOH group increase its acidity. This anomalous behaviour of groups when present in ortho position is termed as **ortho effect** (see page 2·665).

QUESTIONS

A. Essay Type :

1. (*a*) What are the different methods for introducing a carboxyl group into a benzene nucleus ? Give important properties of benzoic acid and explain the term benzoylation.

(*b*) How will you prepare from Benzoic acid—

(*a*) *o*-Toluic acid ; (*b*) Salicylic acid ;

(*c*) Saccharin ? (*Delhi B.Sc. 1972*)

2. How is benzoic acid prepared on a technical scale ? Give its properties. How would you convert benzoic acid into (*a*) benzene ; (*b*) benzoyl chloride ; and (*c*) ethyl benzoate ?

3. **Describe the preparation of cinnamic acid. Give its properties and uses. How would you distinguish between cinnamic acid and benzoic acid ?** *(Ravi Shankar B.Sc. 1972)*

4. **Describe the preparation of cinnamic acid. Give its properties and uses. How would you show that —COOH is not attached to the nucleus and it has an unsaturated side-chain. How would you obtain (*i*) Benzaldehyde (*ii*) Styrene from it** *(Rajasthan B.Sc. 1970)*

5. Give two methods for the synthesis of salicylic acid. What happens when salicylic acid is treated with :

(*a*) Soda lime, (*b*) Neutral ferric chloride solution,

(c) Methyl alcohol with a little H_2SO_4,

(*d*) Acetic anhydride with sodium acetate.

What are the uses of salicylic acid ? *(Nagpur B Sc. 1973)*

6. **How is salicylic acid prepared from phenol ? How can salicylic acid be converted into (*a*) phenol, (*b*) benzoic acid, (*c*) benzene, (*d*) aspirin, (*e*) Salol, (*f*) Benzoic acid, (*g*) Tribromophenol.** *(Delhi B.Sc. Hons Sub. 1977 ; Delhi B Sc 1976)*

7. How will you distinguish between—

(*a*) Salicylic acid and benzoic acid ;

(*b*) Salicylic acid and phenol ?

8. How is cinnamic acid prepared ? Give two examples of the general nature of the reactions involved in its formation. By what chemical tests would you distinguish benzoic acid, cinnamic acid and salicylic acid ? *(Ravi Shankar B.Sc. 1972 ; Bombay 1975)*

9. (*a*) How is phthalic acid prepared ? Mention its important properties and uses.

(*b*) How are anthranilic acid and phenolphthalein obtained from it ? *(Delhi B.Sc. 1977 ; Agra 1973)*

10. How will you prepare the following :

(*a*) Benzoic acid from (*i*) bromobenzene ; (*ii*) phosgene ; (*iii*) benzyl bromide.

(*b*) *p*-Nitrobenzoic acid from toluene. (*c*) 2, 3-Dihydroxylbenzoic acid

(*d*) *m*-Nitrocinnamic acid. (*e*) *o*-Benzoylbenzoic acid.

11. How will you distinguish between the following :

(*a*) Phthalic acid and terephthalic acid.

(*b*) Mandelic acid and *o*-hydroxyphenylacetic acid.

(*c*) *p*-Chlorobenzoic acid and benzoyl chloride.

(*d*) Benzoic acid. *p*-amino-benzoic acid and benzamide.

12. (*a*) Write in detailed equations the method you will use for the preparation of benzoic acid by starting from the following :

(*i*) Benzyl alcohol, (*ii*) Toluene, (*iii*) Aniline, (*iv*) Pheylmagnesium bromide

(*b*) What reactions does it undergo with the following :

(*i*) PCl_5, the product treated with $H_2/Pd\text{-}BaSO_4$

(*ii*) PCl_5, the product treated with aniline,

(*iii*) Ethyl alcohol/H^+, the product treated with $LiAlH_4$? *(Delhi B Sc. 1979 Supp)*

B Short Answer Type :

1. Give one method of preparation for each of the following :

(*a*) Benzoic acid (*b*) Cinnamic acid

(*c*) Salicylic acid. (*d*) Phthalic acid,

2. What happens when :

(*a*) Benzoic acid is distilled with acetic anhydride ;

(*b*) Salicylic acid is treated with phosphorus pentachloride ;

(*c*) Cinnamic acid is treated with chromic acid ; and

(*d*) Phthalic acid is heated with ammonia ? *(Kerala B.Sc. 1972)*

3. Give a brief account of the chemistry of salicylic acid. *(Sri Venkateshwara B.Sc. 1972)*

4. **What happens when benzoic acid is nitrated ?** *(Delhi B.Sc. Hons. Sub. 1977)*

5. How will you convert phthalic acid into :
(*i*) anthranilic acid, (*ii*) benzoic acid and (*iii*) fluorescein ?
(*Agra B.Sc. 1973*)

6. Give the mechanism of Kolbe-Schmitt reaction.

7. Assign reasons for the observation that mesitylenic acid undergoes esterification readily whereas mesitoic acid does not at all undergo esterification.

8. How is coumarin obtained from salicylic acid ?

9. How is salicylic acid obtained from phenol ?

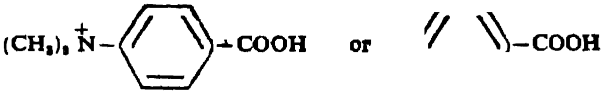
How will you convert this acid into :
(*i*) Benzene, (*ii*) 2,4,6-Tribromophenol,
(*iii*) Benzoic acid and (*iv*) Acetylsalicylic acid ?
(*Kurukshetra B.Sc. 1977 Supp.*)

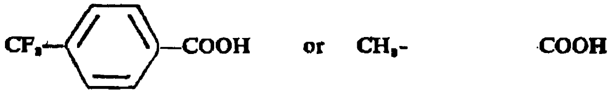
10. Give the reactions involved and name the products formed when cinnamic acid is (*i*) heated, (*ii*) catalytically hydrogenated, (*iii*) treated with potassium permanganate and (*iv*) nitrated. (*Delhi B.Sc. 1977 Supp.*)

11. Arrange in the decreasing order of acidity in the following sets and explain your choice of the order in each case.

(*a*) α-chloropropionic acid, β-chloropropionic acid and propionic acid.
(*b*) *p*-nitrobenzoic acid, *p*-chlorobenzoic acid and benzoic acid
(*c*) *p*-chlorobenzoic acid, *m*-chlorobenzoic acid and benzoic acid
(*d*) *p*-hydroxybenzoic acid, *m*-hydroxybenzoic acid and benzoic acid
(*e*) *p*-nitrobenzoic acid, *m*-nitrobenzoic acid and benzoic acid.

12. Which acid of each pair in the following would you expect to be stronger :

(*i*)


(*ii*)


13. When excess of CO_2 is passed into a solution of sodium benzoate and sodium 4-methylphenoxide in aqueous sodium hydroxide, 4-methyl-phenol separates as an oily liquid while sodium benzoate remains in solution. Explain.

14. Explain how you would separate a mixture of benzoic acid, *p*-cresol and cyclohexanol. You are provided with the following reagents : aq NaOH, aq HCl, ether and CO_2.

C. Problems :

1. A substance A shows the following % composition : C=70·6 H=5·87% and O=23·53%. Its vapour density is 68. When treated with PCl_5 and subsequently with NH_3, A gives a substance B. When reacted with Br_2 and KOH, B forms a base C which on diazotisation and boiling with water gives 2-methyl-benzenol. What are A, B and C ? Explain the reactions.

2. An organic diabasic acid A gave on analysis :
C=57·8%, H=3·6%. Its silver salt contained 56·8% Ag. On heating (A) gives a product (B) $C_8H_4O_3$ which reacts with amm. carbonate to give (C) $C_8H_5O_2N$. Compound (C) forms potassium salt with alc. KOH and is converted into *o*-aminobenzoic acid with NaClO. Assign structure to A, B and C.

3. An organic compound (A) containing 72% carbon and 6·67% hydrogen was refluxed with potassium hydroxide solution till the oily layer disappeared completely. The mixture was then distilled and the distillate gave the iodoform test. On acidification with hydrochloric acid the residue gave a white precipitate (B). The compound (B) contained 68·85% carbon and 4·92% hydrogen. The molecular weight of A is 150.

From the above data and reactions, indicate the nature of the compounds (A) and (B) and name them.

ANSWERS

A, 10. Hints. (*a*)—(*i*) $C_6H_5Br \longrightarrow C_6H_5MgBr \xrightarrow{CO_2} C_6H_5COOH$.

(*ii*) $C_6H_6 + COCl_2$ (*excess*)$+ AlCl_3 \longrightarrow$ followed by hydrolysis.

(*iii*) Oxidation with $KMnO_4$.

(*b*) Nitration—Separation of *o*- and *p*-deriv. by fractional distillation—oxidation of *p*-isomer.

(*c*) 1, 2-Benzenediol+CCl_4+alkali—followed by hydrolysis.

(*d*) $C_6H_5CHO \xrightarrow{\text{Nitration}}$ *m*-Nitro-deriv. $\longrightarrow$ with acetic anhydride and sod. acetate (*Perkin's reaction*).

(*e*) C_6H_6+phthalic anhydride+$AlCl_3$.

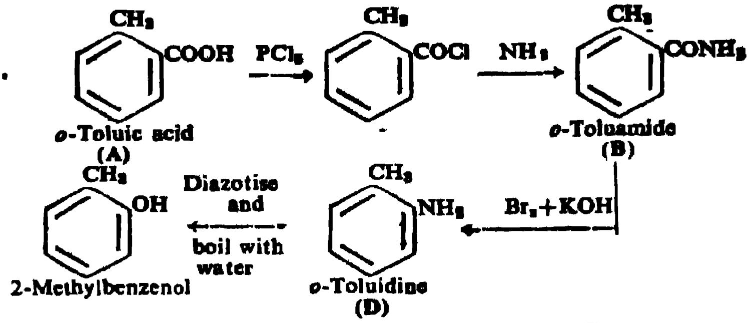
11. Hints : (*a*) Phthalic acid gives an anhydride, the other does not.

(*b*) The latter acid gives tests of a phenol and is brominated with bromine water.

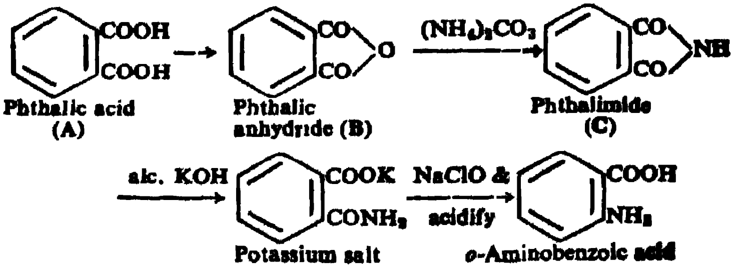
(*c*) The former dissolves in $NaHCO_3$ solution with effervescence. The latter reacts with $AgNO_3$ on standing to give white ppt. of AgCl.

(*d*) The first is acidic, the second is amphoteric, while the third is neutral.

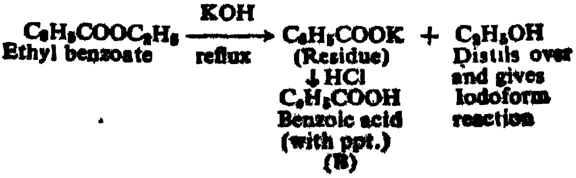
C, 1.



2,



3, (A) is ethyl benzoate, $C_6H_5COOC_2H_5$;
(B) is benzoic acid, C_6H_5COOH.



$$\underset{\text{Ethyl benzoate}}{C_6H_5COOC_2H_5} \xrightarrow[\text{reflux}]{KOH} \underset{\text{(Residue)}}{C_6H_5COOK} + \underset{\substack{\text{Distils over}\\\text{and gives}\\\text{Iodoform}\\\text{reaction}}}{C_2H_5OH}$$

$$\downarrow HCl$$

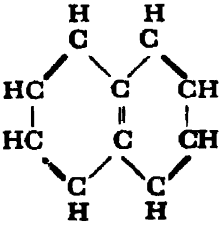
$$\underset{\substack{\text{Benzoic acid}\\\text{(with ppt.)}\\\text{(B)}}}{C_6H_5COOH}$$

PART IV—POLYNUCLEAR HYDROCARBONS

1

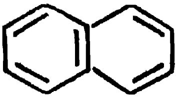
Naphthalene and its Derivatives

1. **Introductory.**—Condensed nuclear compounds are compounds in which two or more carbon atoms are shared in common by two or more aromatic rings. Common examples of this type of compounds are naphthalene, anthracene, and phenanthrene and their derivatives. In naphthalene two carbon atoms are shared in common by two benzene rings as shown below :

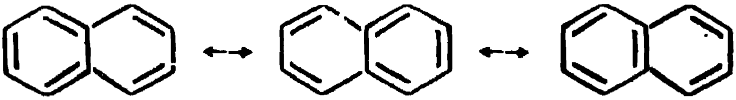


Naphthalene

or

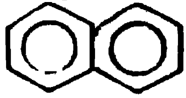


Napthalene is a resonance hybrid of mainly the following three resonating structures :

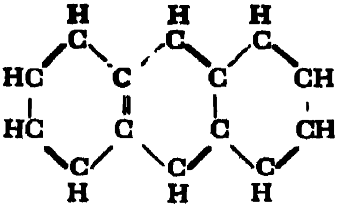


I II III

The resonance hybrid structure of naphthalene is represented for the sake of convenience by two regular hexagons joined together and each containing a circle as given in the margin. This means a resonance hybrid of I to III.

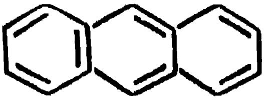


In anthracene three benzene rings are fused together.

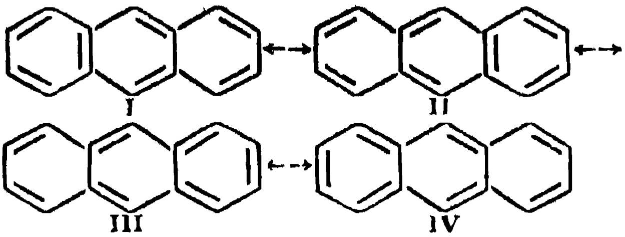


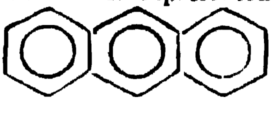
Anthracene

or



Anthracene is a resonance hybrid of the following resonating structures :

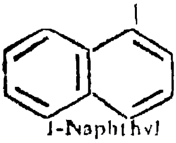


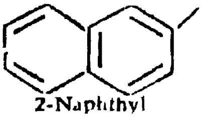


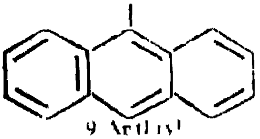
The resonance hybrid structure of anthracene is represented for the sake of convenience by three regular hexagons joined together and each containing a circle as given in the margin. This represents anthracene as a resonance hybrid of I to IV.

It may be noted that for a polynuclear hydrocarbon containing *n* benzene rings fused together in a linear manner, there are $(n + 1)$ canonical forms of the resonance hybrid. Thus naphthalene with two benzene rings fused together has 3 resonating structures and for anthracene with three benzene rings fused together there are four resonating structures.

Substituting univalent groups derived from naphthalene, anthracene and phenanthrene are called naphthyl, anthryl and phenanthryl respectively. The carbon atom having free bond is given the lowest possible number consistent with fixed numbering of the hydrocarbon. For example,


1-Naphthyl

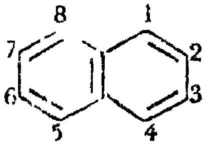

2-Naphthyl

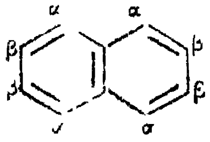

9-Anthryl

NAPHTHALENE

2 Nomenclature and Isomerism of Naphthalene Derivatives.—The carbon atoms of the two rings constituting the molecule of naphthalene are numbered as given below and the position of various substituents is indicated by these numbers.

It will be clear from the formulae given below that the position 1, 4, 5, 8, are equivalent due to symmetry of the molecule and are





denoted by α. Similarly positions 2, 3, 6 and 7 are denoted by β. Thus there are two isomeric mono-substituted (α, β) naphthalenes. Di-substitution products are known as *ortho*, *meta* and *para* like benzene derivatives when two substituents are present in the same ring. 1 : 8 or 4 : 5 position is called *peri*-position, it is also termed αα′ disubstitution product. 2 : 6 or 2 : 7 position is called ***amphi*-position** ; it is also termed ββ′-disubstitution product.

Derivatives of naphthalene show isomerism. Number of possible isomers in mono-, di- and trisubstitution product is given below :

Substituted naphthalene	*No. of isomers*	*Names*
$C_{10}H_7X$ (mono)	2	1 or α ; 2 or β.
$C_{10}H_6X_2$ (Di-)	10	1, 2 ; 1, 3 ; 1, 4 ; 1, 5 ; 1, 6 ; 1, 7 ; 1, 8 ; 2, 3 ; 2, 6 ; 2, 7.

and so on

Thus two mono-, ten di- and fourteen trisubstituted naphthalenes are possible. The number of di- and trisubstitution products increases to 14 and 84 respectively when the substituents are different

3 Manufacture of Naphthalene.

—Naphthalene, $C_{10}H_8$ is the largest single constituent of coal-tar. It constitutes about 6-10% of coal-tar and is present in the middle oil fraction of coal-tar distillation On allowing the middle oil to cool, major portion of naphthalene crystallizes out and is separated by centrifugation or by pressing out the oil in a hydraulic press. The crystals are washed with hot water and with aqueous sodium hydroxide in a centrifugal machine to remove adhering oil and phenols. It is then washed with a little concentrated sulphuric acid which removes the basic impurities. Crude naphthalene is purified by sublimation. For further purification it may be recrystallized from petroleum ether The modern tendency, however, is to replace the 'hot-pressing process' by another involving continuous washing or distillation.

It is interesting to note that naphthalene does not occur in low temperature carbonisation tar

At present naphthalene is also being obtained synthetically from petroleum by passing petroleum fractions over a heated catalyst (e g , copper) at 950K under atmospheric pressure. A mixture of naphthalene and methylnaphthalene is obtained. The latter is converted into naphthalene by **hydro-dealkylation** (by heating with hydrogen under pressure in presence of a metal oxide catalyst).

4 Properties of Naphthalene.

Physical. It crystallizes as colourless lustrous plates (m.p. 353K) having a strong characteristic odour. It is very volatile and readily sublimes on heating. It is insoluble in water but very soluble in ether, benzene and hot alcohol.

Chemical. Chemically naphthalene resembles benzene in many of its reactions. It is, however, more reactive and forms substitution products more readily than benzene. It is found to be somewhat less aromatic than benzene. For example, like alkenes, it forms addition products readily than does benzene. But as soon as one of the rings is saturated (by addition of hydrogen or halogens) or destroyed by oxidation, the second ring is as stable as benzene ring.

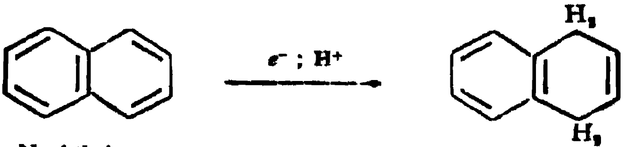
This is explained in the light of its resonance energy. Resonance energy of benzene is 150·6 kJ mol^{-1}. Naphthalene with two benzene rings can be expected to have resonance energy close to 351·2(2 × 150·6) kJ mol^{-1}. Its resonance energy is actually 255·2 kJ mol^{-1}, *i.e.*, each ring in naphthalene has a resonance energy of 127·6 kJ mol^{-1}. Consequently naphthalene has less aromatic character than benzene and is, therefore, more reactive.

Important reactions of naphthalene are :

ADDITION REACTIONS

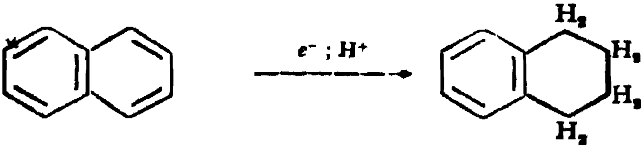
(1) **Addition of Hydrogen.** Naphthalene gives a number of reduction products depending upon the nature of the reducing agent. For example,

(*i*) *With sodium and alcohol* it gives 1, 4-dihydronaphthalene (1, 4-dialin, m.p. 298K).



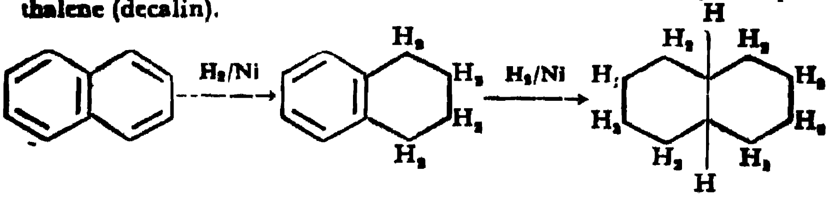
Naphthalene 1, 4-Dialin

(*ii*) *With sodium and isopentanol* it gives 1, 2, 3, 4-tetrahydronaphthalene (tetralin, b.p. 479-481K).



Tetralin

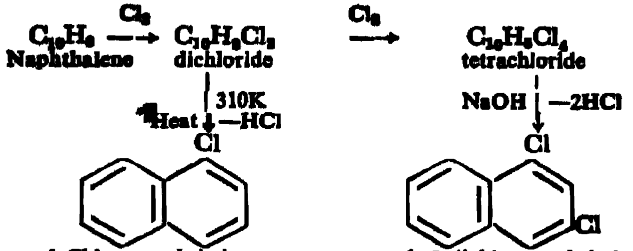
(*iii*) *On catalytic reduction* using nickel it gives decahydronaphthalene (decalin).



Tetralin Decalin

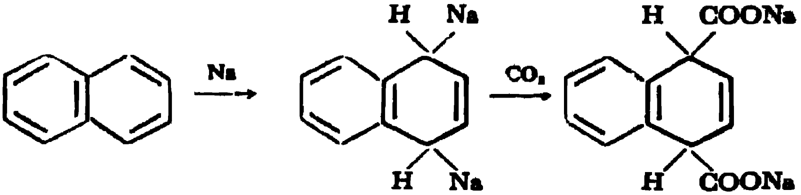
(2) **Addition of Chlorine.** Solid naphthalene reacts with dry chlorine to give addition products—naphthalene di- and tetra-chlorides, $C_{10}H_8Cl_2$ and $C_{10}H_8Cl_4$. Both of them give phthalic acid on oxidation. This shows that the halogen atoms are present in the same ring.

On heating naphthalene dichloride to 310K it loses one molecule of hydrogen chloride and we get 1-chloronaphthalene. Naphthalene tetrachloride on treatment with alkali gives dichloronaphthalene (mainly 1, 3-isomer).



1-Chloro-naphthalene   1, 3-dichloronaphthalene

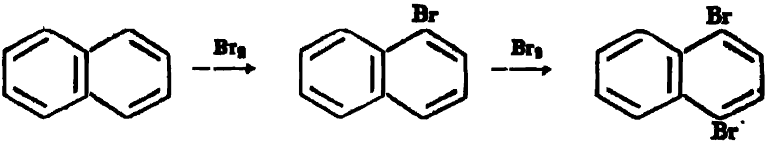
(3) **Addition of Sodium.** With sodium it gives 1, 4-disodionaphthalene which reacts with carbon dioxide to form the sodium salt of 1, 4-dihydronaphthalene-1, 4-dicarboxylic acid.



1, 4-disodio-naphthalene   Sod. salt of 1, 4-dihydro-naphthalene-1, 4-dicarboxylic acid

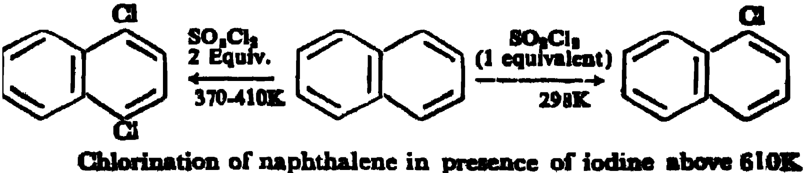
ELECTROPHILIC SUBSTITUTION REACTIONS

(4) **Halogenation.** On bromination in boiling carbon tetrachloride solution, naphthalene gives 1-bromonaphthalene. On further bromination it gives mainly the 1 : 4-dibromonaphthalene with a little of 1 : 2-derivative.

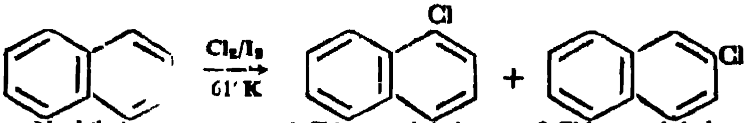


Naphthalene   1-Bromo-naphthalene   1 : 4-Dibromo-naphthalene

Chlorination can be carried on with sulphuryl chloride in presence of aluminium chloride. One equivalent of SO_2Cl_2 at 298K gives 1-chloroderivative whereas two equivalents of SO_2Cl_2 at 370-410K give 1 : 4-dichloronaphthalene.

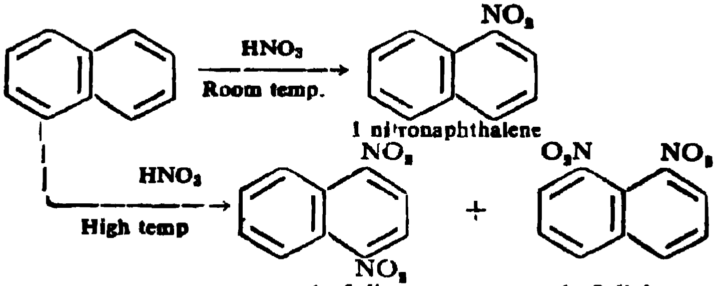


Chlorination of naphthalene in presence of iodine above 610K gives a mixture of two monochloro derivatives, 1- and 2-chloronaphthalene in the ratio 1 : 1.



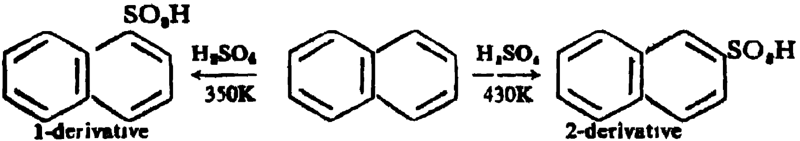
Naphthalene 1-Chloronaphthalene 2-Chloronaphthalene

(5) **Nitration** Naphthalene reacts with nitric acid at room temperature and gives 1-nitronaphthalene. At higher temperature a mixture of 1 : 5- and 1 : 8 dinitronaphthalenes is obtained.



1 : 5-dinitro-naphthalene 1 : 8-dinitro-naphthalene

(6) **Sulphonation.** The main product of sulphonation with concentrated sulphuric acid at 350K is 1-naphthalenesulphonic acid. At 430K, the main product is 2-naphthalenesulphonic acid.



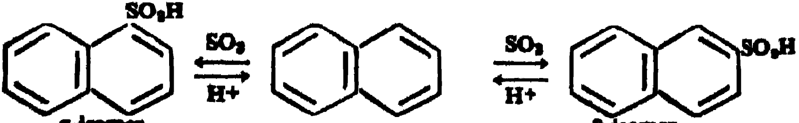
1-derivative (yield—96%) 2-derivative (yield—85%)

1-acid on heating with concentrated sulphuric acid changes into 2-isomer.

These facts can be explained as follows :

Sulphonation is a reversible reaction and like nitration and halogenation occurs more rapidly at the α-position, since this involves the more stable intermediate carbocation. But for the same reason, attack by hydrogen ion resulting in desulphonation also occurs more rapidly at the α-position. Sulphonation at the β-position occurs very slowly but once formed, the β-sulphonic acid tends to resist desulphonation.

At low temperature desulphonation is slow and if the reaction is stopped long before equilibrium is reached, the, α-product, which is formed faster, is isolated. At higher temperature desulphonation becomes important and equilibrium is readily established. At higher temperatures the product isolated is the one that is more stable, *e.g.*, β-naphthalenesulphonic acid.



α-isomer *Formed rapidly ; desulphonated rapidly.*

β-isomer *Formed slowly ; desulphonated slowly.*

The reason for the greater stability of 2-acid is, however, uncertain. One explanation given is that there is steric repulsion in 1-acid from the hydrogen atom present in 8-position.

Fig. 45·1 is the energy profile of the sulphonation of naphthalene (shown as N). Formation of 1-acid (1-S) and 2-acid (2-S) are both exothermic reactions with heats of reaction ΔH_1 and ΔH_2 and activation energies E_1 and E_2 respectively. Rate constants of the two reactions are k_1 and k_2.

1-S being the kinetically controlled product,

$$k_1 > k_2 \text{ and } E_2 > E_1$$

On the other hand 2-S being the thermodynamically controlled product

$$\Delta H_2 > \Delta H_1$$

Activation energy of the desulphonation reaction of 2-acid, $E_{-2} = E_2 + \Delta H_2$ and that of 1-acid, $E_{-1} = E_1 + \Delta H_1$.

As stated above $E_2 > E_1$ and $\Delta H_2 > \Delta H_1$. Hence $E_{-2} >> E_{-1}$. Consequently among the rate constants of the reverse (desulphonation) reactions, $k_{-1} >> k_{-2}$. This explains why 1-acid is formed more rapidly and desulphonated more rapidly than 2-acid.

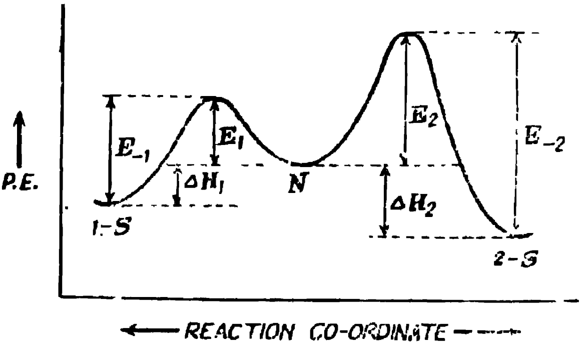
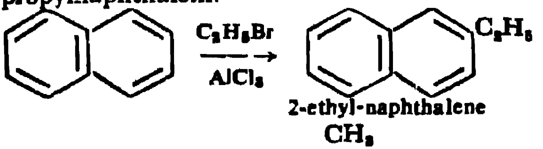
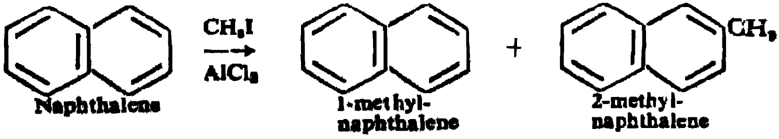


Fig. 45·1—Energy profile of the sulphonation of naphthalene.

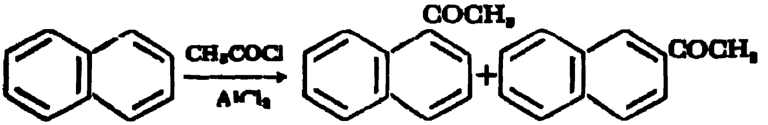
(7) **Friedel-Crafts reaction.** This reaction is carried out in the presence of anhydrous aluminium chloride at low temperatures as under vigorous conditions one of the naphthalene rings opens.

(*i*) ***With methyl iodide,*** 1- and 2-methylnaphthalenes are obtained ***Ethyl bromide*** gives only 2-ethylnaphthalene and *n*-propyl bromide give 2-isopropylnaphthalein.





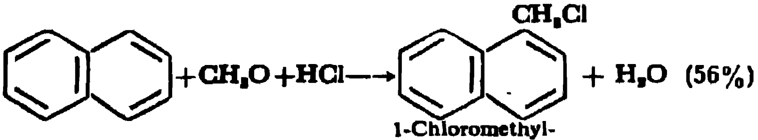
(*ii*) ***With acetyl chloride*** a mixture of 1- and 2-naphthyl methyl ketones is obtained. The composition of mixture is determined by the nature of the solvent used. For example, in CS_2 solvent at 260K the 1- and 2-derivatives are in the ratio 3 : 1 while in nitrobenzene solvent at 298K these are in the ratio 1 : 9.



Naphthalene **1-naphthyl methyl ketone** **2-naphthyl methyl ketone**

The effect of nitrobenzene as solvent has been attributed to its forming a complex with acid chloride and aluminium chloride, which because of its bulkiness, attacks the roomier β-position.

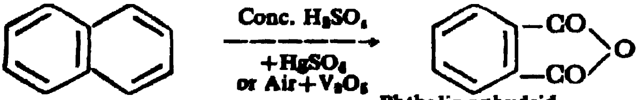
(8) **Chloromethylation.** With a mixture of paraformaldehyde, hydrochloric acid, glacial acetic acid and phosphoric acid naphthalene gives 1-chloromethylnaphthalene (main product) with small amount of 1 : 5-bischloromethylnaphthalene.



1-Chloromethyl-naphthalene

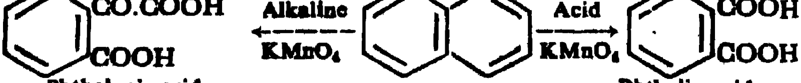
(9) **Oxidation.** Naphthalene undergoes oxidation and the oxidation product depends on the nature of the oxidising agent. For example,

(*i*) ***With concentrated sulphuric acid and mercuric sulphate*** or ***air in presence of vanadium pentoxide*** it is oxidised to ***phthalic anhydride.***



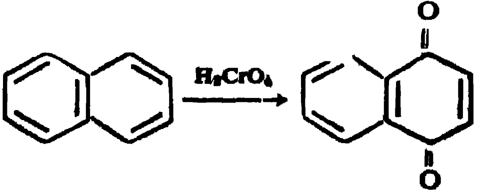
Phthalic anhydride

(*ii*) ***Potassium permanganate*** in acid solution oxidises it to ***phthalic acid*** while in ***alkaline*** solution it oxidises it to ***phthalonic acid***



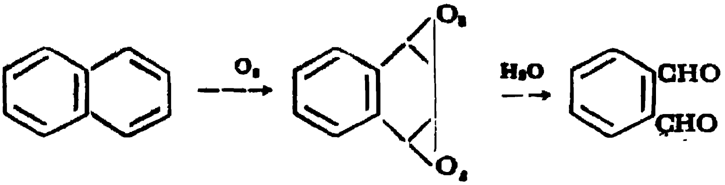
Phthalonic acid **Phthalic acid**

(*iii*) ***With chromic acid*** the oxidation product is 1 : 4-***naphthaquinone.***



1 : 4-naphthaquinone

(*iv*) ***With ozone* naphthalene gives the diozonide which on treatment with water gives phthalaldehyde.**



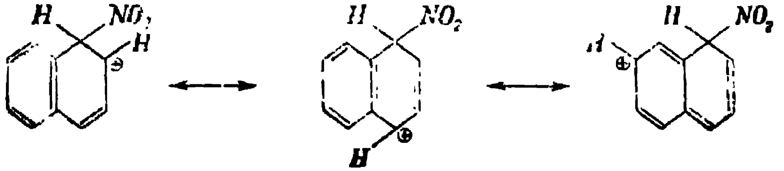
Naphthalene **Diazonide** **Phthalaldehyde**

5. Orientation of Electrophilic Substitution in Naphthalene.—Nitration and halogenation of naphthalene take place almost exclusively in the α-position. We can account for this observed orientation on the following basis :

(*i*) The controlling step in this electrophilic substitution is the attachment of an electrophilic reagent to the aromatic ring to form an intermediate carbocation ; and

(*ii*) This attachment takes place in such a way as to yield the most stable intermediate carbocation. The most favourable structures for the carbocation are those which have one ring fully aromatic.

In the nitration of naphthalene attack by nitronium ion at the α-position of naphthalene yields an intermediate carbocation that is a hybrid of two stable structures I and II, and several unstable structures like III.

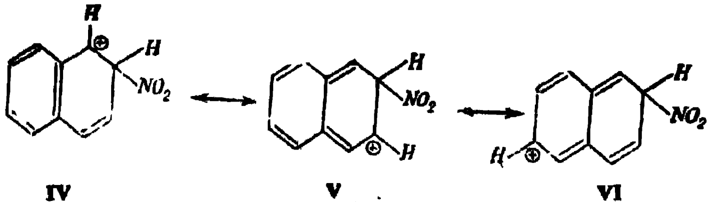


I
More stable
(aromatic sextet
preserved)

II
More stable
aromatic sextet
preserved)

III
Less stable
(aromatic sextet
disrupted)

Attack at β-position yields an intermediate carbocation that is a hybrid of IV and V, and several other structures like VI. Out of these only structure IV is stable in which the aromatic sextet is preserved.



IV
More stable
(aromatic sextet
preserved)

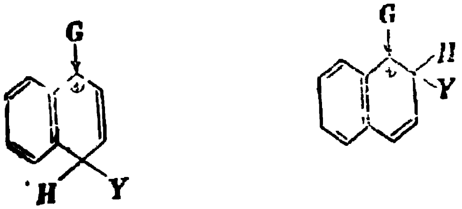
V
Less stable
(aromatic sextet
disrupted)

VI
Less stable
(aromatic sextet
disrupted)

There are two stable contributing structures (I and II) for attack at 1-position while there is only one (IV) for attack at 2-position. On this account the carbocation resulting from attack at 1-position is much more stable than the carbocation resulting from attack at 2-position. Nitration would, therefore, occur much more rapidly at the α-position

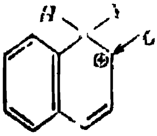
When an electron-releasing group *G* occupies position 1, it directs the attack at position 4 or 2. An electron-releasing group located at position 2 directs the attack at position 1.

On the other hand, an electron-withdrawing deactivating) group at position 1, directs the attack at position 5 in the other ring, because the ring in which it is present is deactivated and hence less prone to electrophilic substitution.

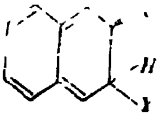


G is the electron-releasing (activating) group located in position 1, it directs attack to position 4 or 2

G is electron-withdrawing (deactivating group) in position 1 and it directs attack to position 5 (other ring)



More stable (aromatic sextet preserved)



Less stable (aromatic sextet disrupted)

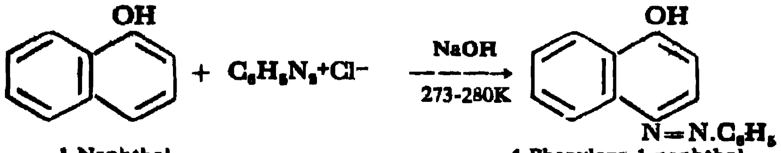
G is electron-releasing (activating) group present in position 2, it directs attack to position 1.

The following two rules which follow from the above discussion can be used to predict the major products of further substitution in a monosubstituted naphthalene :

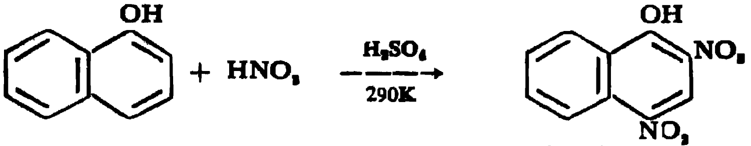
(*a*) An activating group (electron-releasing group) tends to direct further substitution into the same ring. When present in position 1, it directs further substitution to position 4 (and to a lesser extent to position 2). On the other hand when it is present in position 2, it directs further substitution to position 1.

(*b*) A deactivating group (electron-withdrawing group) tends to direct further substitution into the other ring—at an α-position in nitration or halogenation or at an α- or β-position (depending upon temperature) in sulphonation. For example

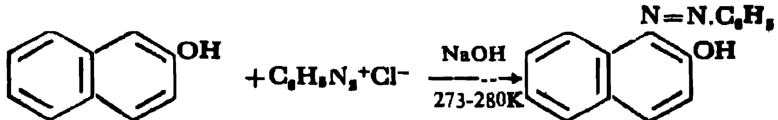
(*i*) Substitution in 1- or 2-naphthol containing an activating or electron-releasing group, OH.



1-Naphthol 4-Phenylazo-1-naphthol

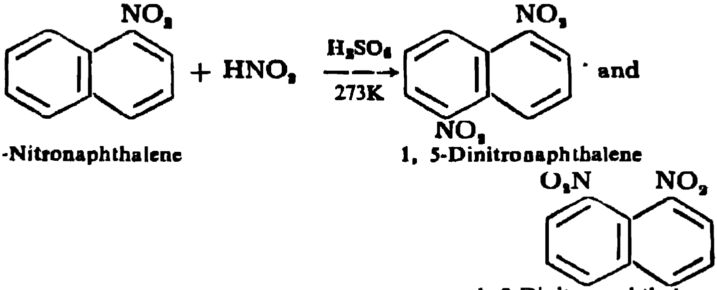


2, 4-Dinitro-1-naphthol



2-Naphthol 1-Phenylazo-2-naphthol

(*ii*) Substitution in 1-nitronaphthalene containing electron-withdrawing or deactivating group NO_2.



1-Nitronaphthalene 1, 5-Dinitronaphthalene

1, 8-Dinitronaphthalene
(*chief product*)

These rules do not always hold in sulphonation, since the reaction is reversible and at high temperature tends to take place at a β-position (*see* page 3·6 for reasons).

Exercise. (*a*) Write structural formulae and names for the predicted products in the following reactions :

(*i*) 1-methylnaphthalene $+Br_2$
(*ii*) 1-methylnaphthalene $+HNO_3+H_2SO_4$
(*iii*) 1-methylnaphthalene $+CH_3COCl+AlCl_3$
(*iv*) The above three reactions with 2-methylnaphthalene
(*v*) 2-nitronaphthalene $+ Br_2$
(*vi*) 2-methoxynaphthalene$+Br_2$.

---

6. Uses.—Naphthalene is considered to be of great industrial value due to the following uses to which it is put :

(*i*) It is used as an insecticide and for preventing moths in clothes. It is, however, now being replaced by more powerful new insecticides such as DDT and *p*-dichlorobenzene.

(*ii*) Large quantities are used in industry for the manufacture of various dyestuffs—azo dyes, eosine and indigo. It is also used for manufacturing *phthalic acid, phthalic anhydride, phthalimide, etc.*

(*iii*) To add to the illuminating power of coal gas, it is carburetted with naphthalene.

7. **Constitution of Naphthalene.**—(1) Molecular formula of naphthalene as calculated from its analytical data is $C_{10}H_8$.

(2) It closely resembles benzene in its chemical properties. For example,

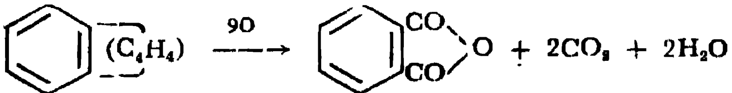
(*i*) It can be chlorinated and sulphonated.

(*ii*) Its amino derivatives can be diazotised and coupled in the usual way.

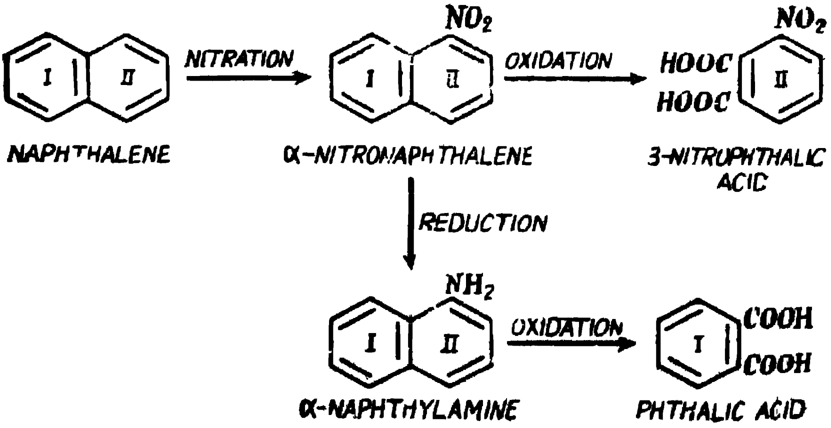
(*iii*) Its hydroxy derivatives exhibit true phenolic character.

This suggests the presence of one or more benzene rings in the molecule.

(3) It resists oxidation under ordinary conditions but gets oxidised on strong heating with conc. H_2SO_4 and a little $HgSO_4$ to produce phthalic anhydride. *This shows the presence of at least one ortho-substituted benzene ring.* The nucleus may be attached in ortho-position to two separate side chains or the two ends of a closed chain. But the former possibility is ruled out by the fact that naphthalene is not highly unsaturated and unstable as required by two side chains. Moreover, the fourth valency of each carbon cannot be explained. So the reaction can be represented by assuming it as some sort of closed chain.



Naphthalene Phthalic anhydride



(4) Naphthalene yields on nitration nitronaphthalene, which on oxidation gives nitrophthalic acid. But if nitronaphthalene is first reduced to aminonaphthalene and then oxidised we get only phthalic acid The above reactions can only be explained by assuming that naphathalene contains benzene rings I and II fused in ortho-position as under :

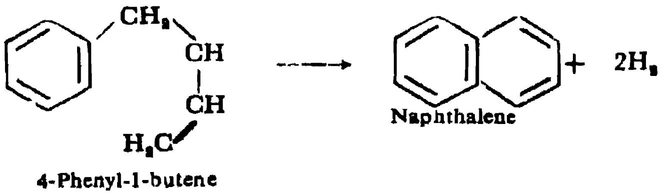
During oxidation of nitronaphthalene the ring I not containing the nitro group is destroyed to yield 3-nitrophthalic acid. An amino group attached to the nucleus renders the latter extremely sensitive to oxidation. So during oxidation of aminonaphthalene, the ring II containing NH_2 group is *destroyed* to give phthalic acid.

The symmetrical formula for naphthalene was proposed by Erlenmeyer in 1866. Graebe proved in 1869 that it did consist of two benzene rings fused together in the ortho-positions.

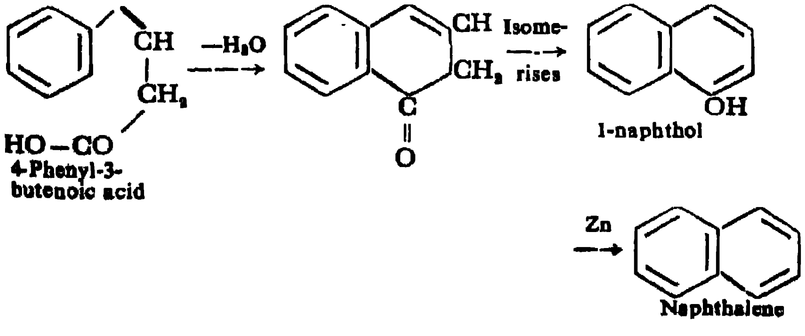
The reason for the difference in behaviour on oxidation is that the nitro group makes an aromatic ring harder to oxidise than an unsubstituted benzene ring, whereas the amino group increases the ease of oxidation of the ring to which it is attached.

(5) The view is further confirmed by various syntheses.

(*a*) When vapours of 4-phenyl-1-butene are passed over red-hot lime, it produces naphthalene with the loss of hydrogen.



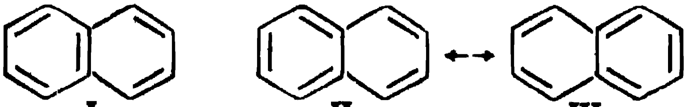
(*b*) α-naphthol is obtained by heating 4-phenyl-3-butenoic acid to 570K. α-Naphthol on heating with zinc dust yields naphthalene,



(6) The formula accounts for the existence of two monosubstitution products, frequently designated as 1- and 2-, and ten -disubstiution products when both groups are alike.

(7) Up to ten hydrogen atoms can be added to naphthalene indicating the presence of five potential double bonds.

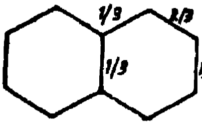
(8) Physico-chemical evidences, *e.g.*, heat of combustion, etc., point towards naphthalene being a resonance hybrid of mainly the following three resonating structures :



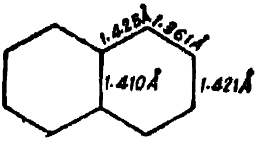
I II III

The resonance energy of naphthalene is 255·2 kJ mol^{-1}.

If we assume that each structure contributes equally to its resonance hybrid, then, in the case of naphthalene, the $C_1—C_2$ bond is double in two structures and single in one while the $C_2—C_3$ bond is single in two structrues and double in one. We would, therefore, expect that the two bonds have $\frac{2}{3}$ and $\frac{1}{3}$ double-bond character, respectively, as shown in IV. Accordingly, the $C_1—C_2$ bond should be shorter than the $C_2—C_3$ bond, and this has been verified by X-ray diffraction studies of crystalline naphthalene. Bond lengths of $C_1—C_2$ bond and $C_2—C_3$ bond are 1·361Å and 1·421Å respectively as shown in V.

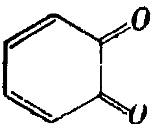


IV



V

Fries Rule (1935). Fries compared the possible arrangements of double bonds in naphthalene with those in benzoquinones. Arrangements in structures II and III correspond to those in *o*-benzoquinone shown in the margin. He believed that since benzoquinones are far more reactive than an aromatic compound, a stable form of a polynuclear compound did not contain an arrangement resembling the one in quinone structure. Based on this arrangement he formulated the rule which is known after his name as Fries rule. It states—



The most stable arrangement of double bonds in a polynuclear compound is the one in which the maximum number of rings possess the benzenoid structure (having three double bonds).

Thus out of the three canonical forms of the resonance hybrid of naphthalene form I with two benzenoid rings is the most stable. Forms II and III with only one benzenoid ring each are not so stable. Naphthalene, therefore, tends to behave as structure (I) rather than as II or III.

Consideration of atomic orbitals shows that ten carbon atoms lie at the corners of two fused hexagons Each carbon atom is attached to three other atoms by σ bonds resulting from the overlapping of trigonal sp^2 orbitals and all carbon and hydrogen atoms lie in a single plane There is a cloud of π electrons formed by the overlapping of p- orbitals and shaped like a figure 8 above and below the plane of carbon atoms. The cloud may be considered as made up of two partially overlapping sextets (π electron clouds containing six electrons) which have a pair of π electrons in common.

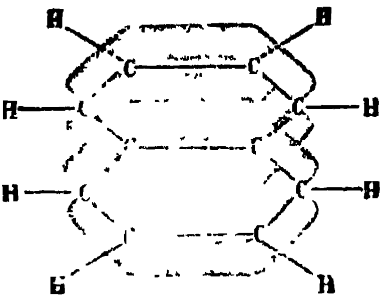
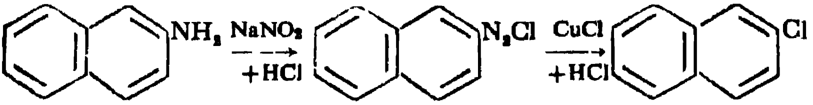


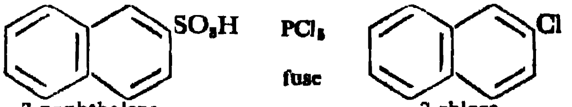
Fig. 1.2—π clouds above and below the plane of rings in the naphthalene molecule.

DERIVATIVES OF NAPHTHALENE

8. **Halogen Derivatives**—Direct halogenation of naphthalene gives 1-chloro- or 1-bromonaphthalene. 2-Halogeno-naphthalenes are prepared from 2-naphthylamine or 2-naphthalenesulphonic acid.



2-naphthylamine 2-naphthalene-diazonium chloride 2-chloronaphthalene

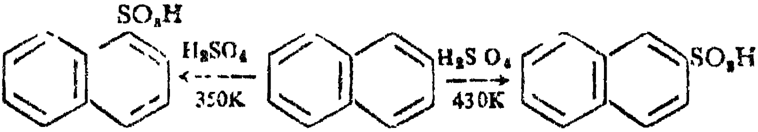


2-naphthalene-sulphonic acid 2-chloro-naphthalene

9. **Nitronaphthalene**—1-Nitronaphthalene (m.p. 333K) is prepared by treating napthalene with concentrated nitric acid at room temperature. It is a yellow solid and resembles nitrobenzene in most of its reactions. It reacts with phosphorus pentachloride to form 1-chloronaphthalene unlike nitrobenzene which does not react with PCl_5.

2-Nitronaphthalene (m p. 352K) is prepared indirectly by heating 2-naphthalenediazonium borofluoride with sodium nitrite and copper powder

10. **Naphthalenesulphonic acid**—Both 1- and 2-naphthalenes sulphonic acids can be prepared by direct sulphonation.



1-deriv. (m p. 433K)
(96%)

2-deriv. (m p. 375K)
(86%)

On treating the mixture with superheated steam, the 1-acid decomposes to give naphthalene while 2-acid remains practically unaffected. Calcium and lead salts of 1-acid are more soluble than those of the 2-acid The isomeric acids may be separated forming those salts.

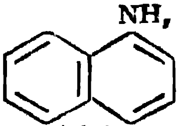
Properties of these acids are similar to those of benzensulphonic acid but the sulphonic group in naphthalenesulphonic acids is more easily replaced. For example,

(*i*) The sulphonic acid group is replaced by —Cl when fused with phosphorus pentachloride and a chloronaphthalene is obtained.

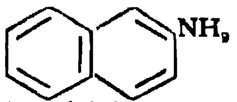
(*ii*) On oxidation with acid permanganate, both the acids give phthalic acid.

(*iii*) 1-Acid changes into the 2-isomer on heating with concentrated sulphuric acid. *2-Acid is the starting material for the preparation of various 2-naphthalene derivatives.*

11. Naphthylamines.—Two isomeric naphthylamines are :

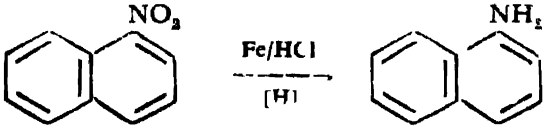


1-naphthylamine



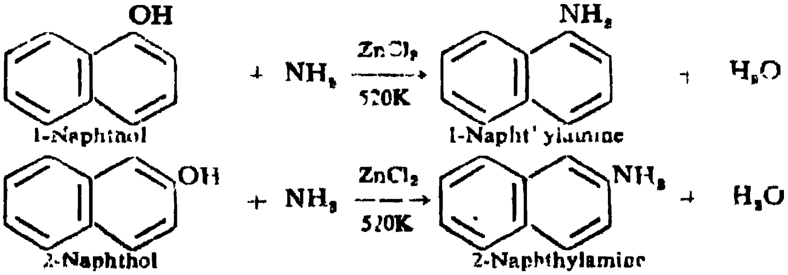
2- naphthylamine

Preparation. (*i*) 1-derivative may be prepared by reducing 1-nitronaphthalene with iron and hydrochloric acid.



The halogen atom in naphthalene behaves similarly as in the benzene ring, but it is more reactive.

(*ii*) Both the isomers can be prepared by heating the corresponding naphthols with a double compound of zinc chloride and ammonia (*Bucherer reaction*).



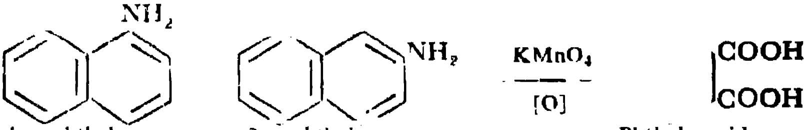
Properties. Both naphthylamines are colourless solids (1-, m.p 323K ; 2-, m.p. 385K) insoluble in water but soluble in alcohol and ether. 1-Isomer has an unpleasant odour and turns red on exposure to air while the 2-derivative is odourless. Their important chemical reactions are :

(i) *Basic nature* They resemble aniline but are weaker bases. They dissolve in acids forming salts. Like aniline they yield diazonium salts which can be coupled with amines and phenols forming dyes.

(ii) *With ammoniacal silver nitrate.* Both of them reduce ammoniacal silver nitrate.

(iii) *With ferric chloride.* Salts of 1-naphthylamine give a blue precipitate with ferric chloride but 2-naphthylamine gives no coloration.

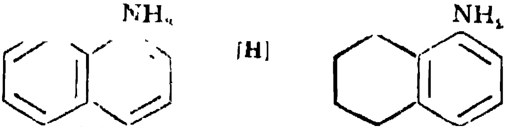
(iv) *Oxidation* Both of them are oxidised to phthalic acid by permanganate



1-naphthylamine 2-naphthylamine Phthalic acid

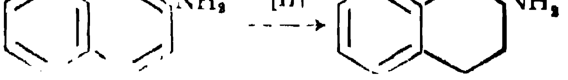
(v) *Reduction* With sodium and isopentanol they behave differently and yield different reduction products.

1-isomer is reduced to *ar*- tetrahydro-1-naphthylamine (5 : 6 : 7 : 8-tetrahydro 1-naphthylamine). The prefix *ar*- indicates that the four hydrogen atoms are not in the ring containing -NH$_2$ group



1-Naphthylamine 5 : 6 : 7 : 8-tetrahydro-1-naphthylamine

2-isomer is reduced to *ac*-tetrahydro-2-naphthylamine (1:2:3:4-tetrahydro-2-naphthylamine) The prefix *ac*- (alicyclic) indicates the four hydrogen atoms are in the ring containing the amino-group.



Naphthylamine 1 : 2 : 3 : 4-tetrahydro-2-naphthylamine

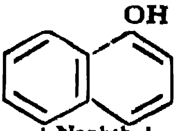
(vi) *Coupling* 1-isomer couples with diazonium salts in the 4-position whereas 2-isomer couples only in the 1-position and no coupling occurs if this position is occupied.

(vii) *Sulphonation.* On heating with concentrated sulphuric acid at 400K, 1-naphthylamine yields naphthionic acid (1-naphthylamine-4-sulphonic acid). This is used in the preparation of Congo-red.

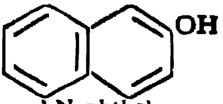
On heating 2-naphthylamine with concentrated sulphuric acid one sulphonic group enters in position 5, 6, 7 or 8 giving four different sulphonic acids according to temperature.

Uses. Naphthylamines are used in the manufacture of dyes.

12. Naphthols.—Monohydroxy derivatives of naphthalene are called naphthols. These are called 1- or 2-naphthol depending upon the position of —OH group in the molecule.



1-Naphthol



2-Naphthol

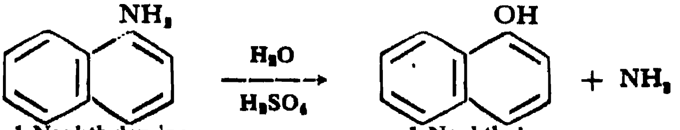
Both of these are present in coal-tar.

Preparation. These are manufactured by *fusing the sodium salt of the corresponding naphthalenesulphonic acids with sodium hydroxide.*

$$C_{10}H_7.\underline{|SO_3Na \quad + \quad Na|}OH \xrightarrow{570K} C_{10}H_7OH + Na_2SO_3 \quad (70\text{-}80\%)$$

1- or 2-sodium naphthalenesulphonate 1- or 2-Naphthol

Pure 1-naphthol is prepared *by heating 1-naphthylamine with dilute sulphuric acid at 560K under pressure.*



1-Naphthylamine 1-Naphthol

Properties. These are colourless crystalline solids (m. pt. 1- =368K ; 2- =395K) with faint phenolic odour. They are sparingly soluble in water but readily dissolve in alkalis forming naphthoxides, *e.g.*, $C_{10}H_7ONa$ (sodium naphthoxide).

Chemically naphthols resemble phenols but the —OH group in naphthol is more readily replaced by other groups than in phenol. Between themselves 2-naphthol is more reactive than 1-naphthol. Important reactions of naphthols are :

(*i*) *With ferric chloride.* 1-Naphthol gives a violet precipitate with ferric chloride whereas 2-naphthol gives a green precipitate.

(*ii*) *With ammonia.* They react with a mixture of aqueous ammonia and ammonium sulphite or with ammonia and zinc chloride to give corresponding naphthylamines.

$$C_{10}H_7\underline{|OH \; + \; H|}NH_2 \xrightarrow{(NH_4)_2SO_3} C_{10}H_7NH_2 \quad + \quad H_2O$$

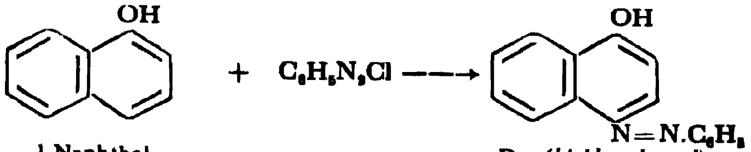
1- or 2-Naphthol 1- or 2-Naphthylamine

(*iii*) *Formation of Ethers.* On heating with an alcohol in presence of concentrated sulphuric acid, naphthols yield ethers.

$$C_{10}H_7OH + C_2H_5OH \xrightarrow[H_2SO_4]{Conc.} C_{10}H_7OC_2H_5$$

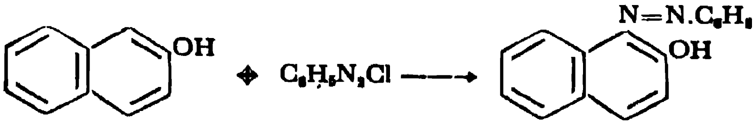
2-Naphthol 2-Naphthyl ethyl ether

(*iv*) *Coupling*. Naphthols couple with diazonium salts. Coupling occurs in position 4 in 1-naphthol and in the adjacent 1-position in case of 2-naphthol. No coupling occurs when this adjacent 1-position is occupied.



1-Naphthol

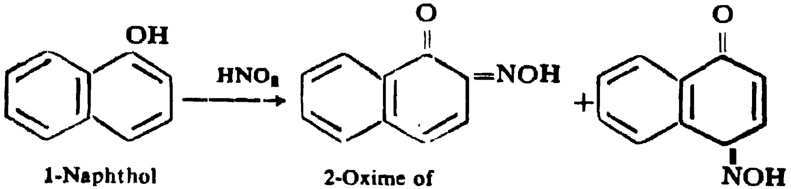
Dye (*highly coloured*)



2-Naphthol

Dye (*highly coloured*)

(*v*) *With Nitrous acid*. 1-Naphthol on treatment with nitrous acid gives mainly 2-oxime of 1, 2-naphthaquinone with small-quantity of 4-oxime of 1, 4-naphthaquinone.

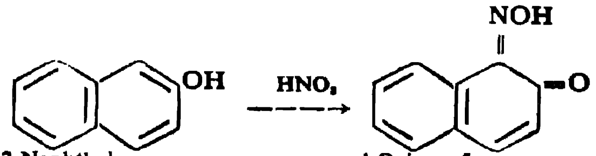


1-Naphthol

2-Oxime of
1, 2-naphthaquinone

4-Oxime of
1, 4-naphthaquinone

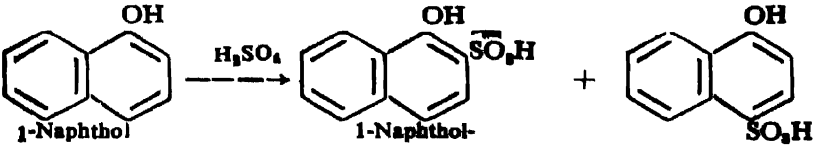
2-Naphthol gives 1-oxime of 1, 2-naphthaquinone and the yield is 99%.



2-Naphthol

1-Oxime of
1, 2-Naphthaquinone

(*vi*) *Sulphonation*. On direct sulphonation under mild conditions 1-naphthol gives a mixture of 1-naphthol-2-sulphonic acid and 1-naphthol-4-sulphonic acid.

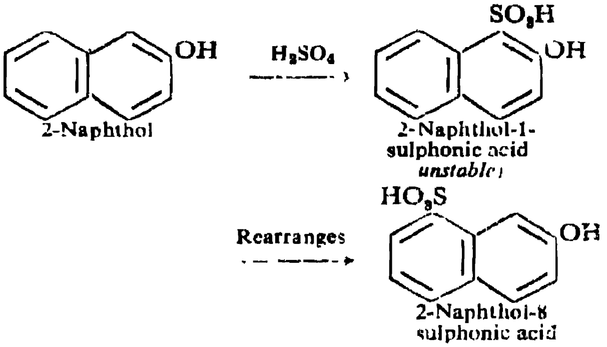


1-Naphthol

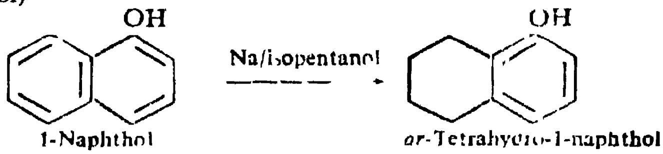
1-Naphthol-
1-sulphonic acid

1-Naphthol-
4-sulphonic acid

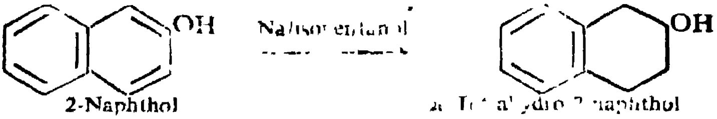
2-Naphthol gives 2-naphthol-1-sulphonic acid which is unstable and rearranges to give 2-naphthol-8-sulphonic acid.


SO$_3$H
OH
H_2SO_4
OH
2-Naphthol
2-Naphthol-1-sulphonic acid unstable)
HO_3S
Rearranges
OH
2-Naphthol-8 sulphonic acid

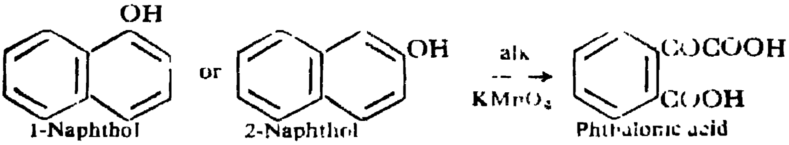
(*vii*) ***Reduction.*** 1-Naphthol on reduction with sodium and isopentanol gives *ar*-tetrahydro-1-naphthol (5 · 6 · 7 : 8-tetrahydro-1-naphthol)



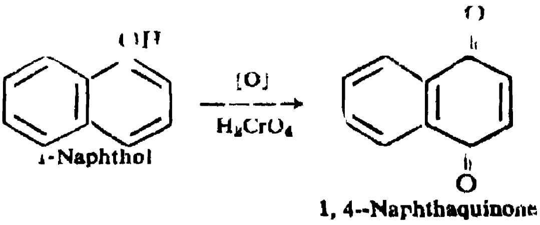
2-naphthol gives mainly *ac*-tetrahydro-2-naphthol (1 · 2 : 3 : 4-tetrahydro-2-naphthol).



(*viii*) *Oxidation* Both 1 and 2-naphthol reduce ammoniacal silver nitrate. Both of them are oxidised by alkaline potassium permanganate to phthalonic acid.



With chromic acid 1-naphthol is oxidised to 1, 4 naptha-quinone

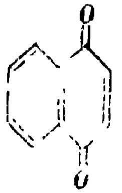


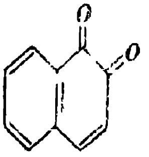
Uses. (*i*) The amino- and sulphonic derivatives of the **naphthols** are used in the manufacture of dyes.

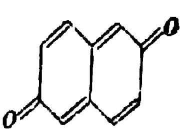
(*ii*) 2-Naphthol has a medical use as an intestinal antiseptic. **Its** derivatives like benzoate and salicylate are also used in medicine.

(*iii*) Its methyl and ethyl ethers are employed in perfumery.

13. Naphthaquinone, $C_{10}H_6O_2$.—Theoretically six naphthaquinones (1 : 2-, 1 : 4-, 1 : 5-, 1 : 7-, 2 : 3- and 2 : 6-) are possible. Only three of these are known and are given below :—

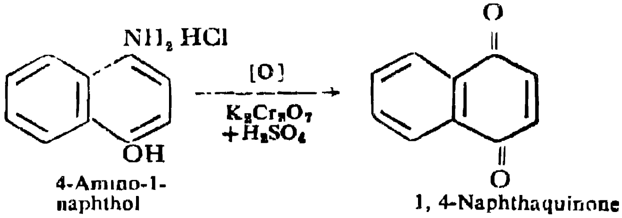






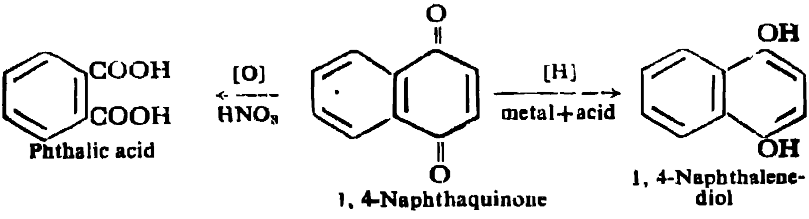
1, 4-Naphthaquinone 1, 2 Naphthaquinone 2, 6-Naphthaquinone

1, 4-**Naphthaquinone** may be prepared by oxidation of 1, 4-naphthalenediamine, 1, 4 naphthalenediol or 4-amino-1-naphthol with acid dichromate.

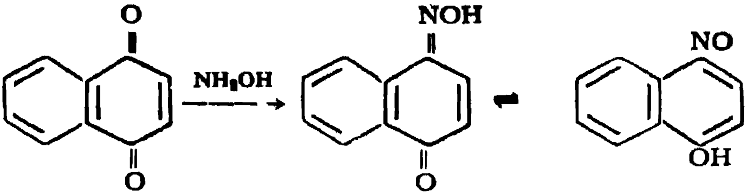


It is a volatile yellow solid (m.p. 398K) having a pronounced odour

Chemically it resembles 1,4-benzoquinone. It is not, however, reduced by sulphurous acid. On reduction with metal and acid, it gives 1, 4-naphthalenediol and on oxidation with nitric acid gives phthalic acid.



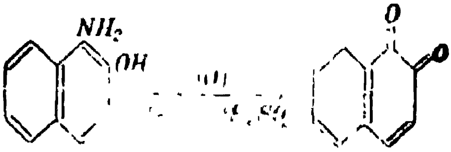
With hydroxylamine, it forms monoxime which is tautomeric with the nitrosophenol form.



Monoxime Nitrosophenol form

Vitamin K is a derivative of 1, 4-naphthaquinone.

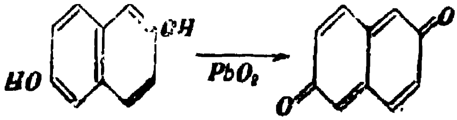
1, 2-**Naphthaquinone** may be prepared by oxidation of 1-amino-2-naphthol with dichromate and sulphuric acid (yield=75%).



1-Amino-2-naphthol 1, 2-Napthaquinone

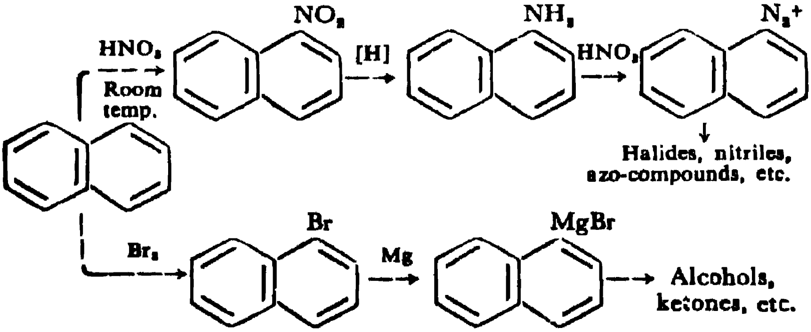
It crystallizes as non-volatile, odourless, red needles and decomposes when heated at 310-340K.

2, 6-**Naphthaquinone** may be obtained by oxidation of 2, 6-naphthalenediol dissolved in benzene with lead dioxide.



It is non-volatile, odourless, orange solid (m.p. 408K).

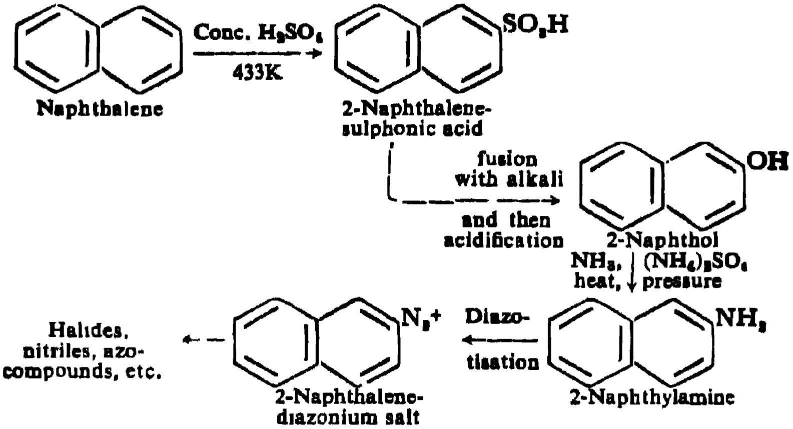
14. Synthesis of 1-substituted naphthalenes.—Procedure for the synthesis of various 1-substituted naphthalenes is summarised below.



Exercise. Write steps for the conversion of naphthalene into :

(*i*) α-naphthonitrile, (*ii*) α-naphthoic acid, (*iii*) 1-naphthyl ethyl ketone, (*iv*) 1-naphthylamine.

15. Synthesis of β-substituted naphthalenes.—Procedure for the synthesis of various β-substituted naphthalenes is given below :


Conc. H_2SO_4
433K
SO_3H
Naphthalene
2-Naphthalene-sulphonic acid
fusion with alkali and then acidification
OH
2-Naphthol
NH_3, heat, $(NH_4)_2SO_4$ pressure
NH_2
Diazo-tisation
2-Naphthylamine
N_2^+
2-Naphthalene-diazonium salt
Halides, nitriles, azo-compounds, etc.

Exercise. (*a*) Write steps for the conversion of naphthalene into (*i*) 2-Bromonaphthalenecarboxylic acid, (*ii*) 2-naphthalenecarbonitrile, (*iii*) 2-naphthalenecarboxylic acid (*iv*) 2-naphthalenecarbaldehyde.

(*b*) Diazonium salts can be converted into nitro compounds by treatment with $NaNO_2$ in presence of a catalyst. Suggest a method for the conversion of naphthalene into 2-nitronaphthalene.

QUESTIONS

A. Essay Type :

1. How is naphthalene prepared ? How many mono- and di- derivatives containing the same group are given by naphthalene ? Give its important properties and uses. (*Calcutta B.Sc. 1972 ; Calicut 1974*)

2. Describe the preparation of naphthalene from coal-tar. Indicate how the following compounds could be prepared from naphthalene :

(*i*) Benzene ; (*ii*) Anthranilic acid ; (*iii*) 1-Naphthol ;
(*iv*) 2-Naphthol ; (*v*) Naphthylamines ; (*vi*) 1-Nitronaphthalene ;
(*vii*) 1-Naphthalenesulphonic acid ; (*viii*) Tetralin ;
(*ix*) 2-Chloronaphthalene.

3. (*a*) Discuss the constitution of naphthalene.
(*Jabalpur B.Sc. 1973 ; Marathwada 1972 ; Delhi 1974, 71 ; Kerala 1973*)

(*b*) How would you prepare Naphthols from Naphthalene ? What is the action of chlorine on Naphthalene ? (*Delhi B.Sc. 1971*)

4 What happens when—

(*a*) 1- and 2 Naphthols are reduced with sodium and isoamyl alcohol ?

(*b*) Naphthalene is treated with chlorine at (*a*) the ordinary temperature, (*b*) high temperature ? Discuss the chemical behaviour of the compound formed.

(*c*) 4-Amino-1-naphthol is treated with acid dichromate.

5. How are the two naphthols prepared ? How are these distinguished ? What is the action of sodium and isoamyl alcohol on them ?

6. Write a short note on electrophilic substitution in naphthalene. (*GND B.Sc. 1982*)

B. Short Answer Type .

1. Write structural formulae for the following ·

(*i*) 1-Nitroso-2-naphthol. (*ii*) 2-Nitroso 1-naphthylamine
(*iii*) 2-Chloronaphthalene (*iv*) 1, 8-Dinitro-2-naphthol.
(*v*) 1, 8-Naphthalenedisulphonic acid (*vi*) 1, 4-Dibromonaphthalene
(*vii*) 1, 8-Dinitronaphthalene. (*viii*) 2, 6-Dinitronaphthalene

2. In which position will benzenediazonium chloride couple with the following :

(*i*) 1-Naphthol. (*ii*) 2-Methyl-1-naphthol (*iii*) 4-Methyl 1-naphthol.
(*iv*) 1-Methyl-2-naphthol (*v*) 2, 7-naphthalenediol
(*vi*) 1, 8-dimethyl-2,7 naphthalenediol
(*vii*) 1-Methyl-2, 7-naphthalenediol.

3 What are the products obtained by reduction, oxidation, halogenation, nitration and sulphonation of naphthalene ? (*Kerala B Sc. 1973*)

4 (*i*) What is the controlling step in the electrophilic substitution in naphthalene ?

(*ii*) What is the most favourable structure of the carbocation obtained in the above step ?

5 State two rules used to predict the major products obtained in further substitution of a monosubstituted naphthalene

6 Give one synthesis of naphthalene

7 Give resonance hybrid structure of naphthalene What is the double bond character of various bonds in naphthalene ?

8 How do you proceed for the synthesis of 2 substituted naphthalenes ?

9 How can naphthalene be converted into (*a*) 2-naphthol, and (*b*) 1-naphthylamine, (*c*) decalin, (*d*) anthranilic acid

(*Delhi B Sc 1980 B Sc Hons Sub 1977, 5*)

10 What is the principal product when

(*a*) 1-Methylnaphthalene is nitrated ?
(*b*) 2-Nitronaphthalene is brominated (*Delhi B Sc Hons 1979*)

11 Write the structure of product in the reaction

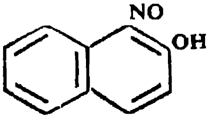
$$\text{Naphthalene}-\begin{cases}\xrightarrow[\text{350K}]{\text{conc } H_2SO_4} ? \xrightarrow[\text{fusion}]{\text{Alkaline}} ?\\[2ex] \xrightarrow[\text{430K}]{\text{Conc } H_2SO_4} ? \xrightarrow[\text{fusion}]{\text{Alkaline}} ?\end{cases}$$

(*Madurai Kamraj B.Sc , 1981*)

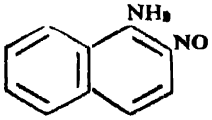
12. A neutral solid (A) has the formula $C_{10}H_7O_2N$ Vigorous oxidation of A gives a dibasic acid (B), $C_8H_5O_6N$ A can be reduced to a compound (C), $C_{10}H_9N$ which on oxidation gives a dibasic acid (D) $C_8H_6O_4$ The compound A can be obtained by direct nitration of a particular aromatic hydrocarbon How would you identify the compounds A to D ? (*Delhi B Sc 1981*)

ANSWERS

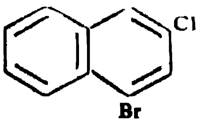
B. 1. (*i*)



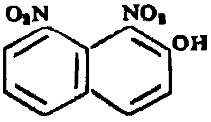
(*ii*)



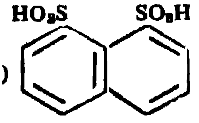
(*iii*)



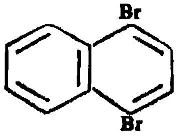
(*iv*)



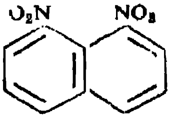
(*v*)



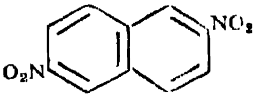
(*vi*)



(vii)

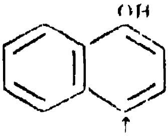


(viii)

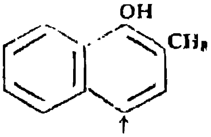


2. The positions where coupling will occur have been indicated by arrows :

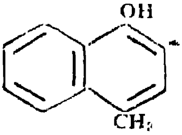
(i)



(ii)

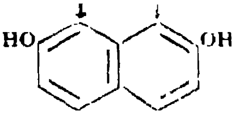


(iii)



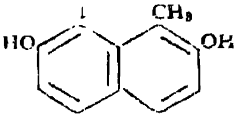
(iv) None

(v)



(vi) None

(vii)

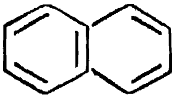


B. 12. See structure of naphthalene (page 3·12)

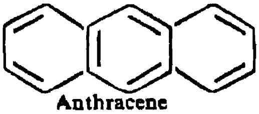
2

Anthracene and its Derivatives

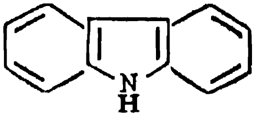
1. Anthracene, $C_{14}H_{10}$.—In the last chapter we have studied about naphthalene, a hydrocarbon having two condensed benzene nuclei. Anthracene is another example of this kind and contains three benzene nuclei fused together in ortho positions.



Naphthalene



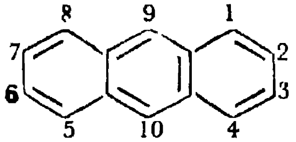
Anthracene

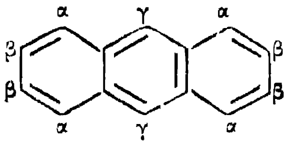


Carbazole

Anthracene is present in coal-tar to the extent of less than half a per cent. It derives its name from the word *anthrax* (Greek = coal). One of the high boiling fractions (540-630K) obtained in the fractional distillation of coal-tar is named anthracene oil as it contains anthracene.

2. Nomenclature and Isomerism of Anthracene Derivatives.—For purposes of naming derivatives of anthracene, its carbon atoms are numbered as follows :





From the formula it is clear that it gives three isomeric monosubstitution products : 1- or α-, 2- or β- and 9- or γ- (or meso). In IUPAC system of nomenclature we make use of only numerals 1, 2, 3 ...and not α, β, γ etc.

There are 15 possible isomeric disubstitution products with two like groups substituted for hydrogen. When the two substituents are not identical, the number of isomers is larger than 15.

3. Preparation of Anthracene.—Coal-tar contains about 0·25-0·45% of anthracene and is the chief source from which it is manufactured. Anthracene is present in the *green oil* or *anthracene oil* (a fraction collected between 540-630K) during coal-tar distillation along with phenanthrene, carbazole and other substances.

On allowing the oil to stand in shallow tanks a viscous mass separates out and crude anthracene (about 20%) is obtained by filtering it through a vacuum filter. This is agitated with light oil at about 360K and filtered again when anthracene content in the cake rises to about 35%. This is heated to 370K and traces of oil removed in a centrifugal machine when about "50 per cent anthracene" is obtained.

The product may further be purified by powdering and washing first with solvent naphtha which dissolves out phenanthrene (*see* page 3·15) and then with pyridine which removes carbazole. Anthracene may finally be crystallized from benzene

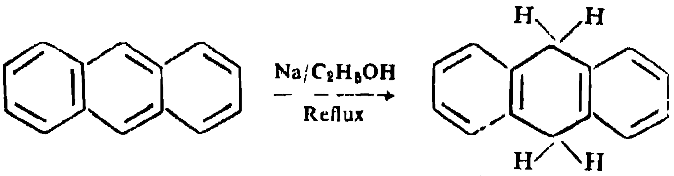
In an *alternative method*, the residue left after the removal of phenanthrene with solvent naphtha, is fused with solid potassium hydroxide. On fusion carbazole gives non-volatile potassio-carbazole. Unreacted anthracene present in the melt is recovered by subliming out.

4. Properties of Anthracene.

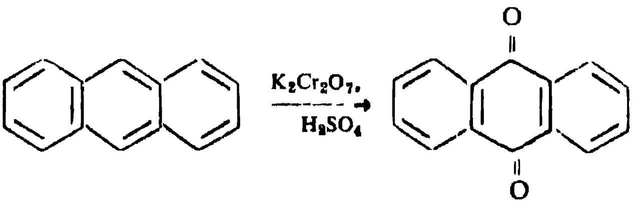
Physical. It is a colourless solid (m.p. 489K) with a blue fluorescence. It is insoluble in water and sparingly soluble in organic solvents. It is comparatively more soluble in hot benzene. With picric acid it forms picrate (m.p. 411K).

Chemical. Anthracene resembles benzene and naphthalene in most respects. It is, however, very reactive in the 9 : 10-positions For example, it is oxidised to 9, 10-anthraquinone and reduced to 9, 10-dihydroanthracene. The orientation of these reactions and the comparative ease with which they take place are understandable on the basis of the structures involved. Electrophilic attack at 1- or 2-position to give σ-complex, leaves a naphthalene ring intact involving a loss of 351·5 - 256·2 96·5 kJ mol^{-1}. On the other hand σ-complex formed by electrophilic attack at 9- and 10-positions leaves two benzene rings intact, thus there is a sacrifice of only 50·2 kJ of resonance energy (351·4 - 2 × 150·6). Obviously the σ-complex formed by attack at 9- and 10-positions is more stable and more readily formed. This explains why anthracene is very reactive in the 9 : 10-positions.

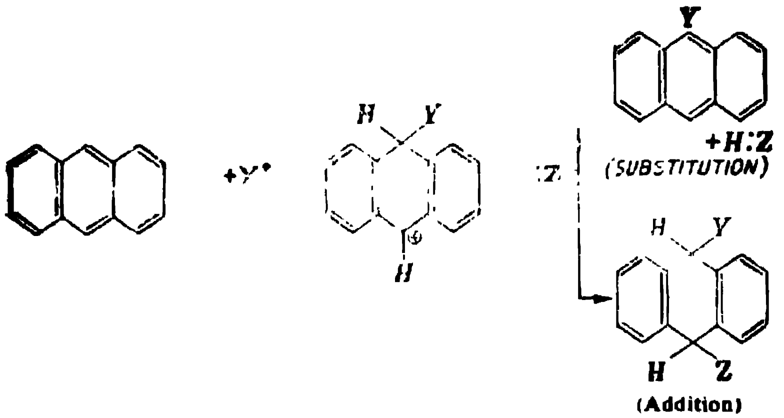
In general, *for polynuclear aromatic hydrocarbons the σ-complex with maximum number of isolated benzene rings is the most stable.*



9, 10-Dihydroanthracene



9, 10-Anthraquinone

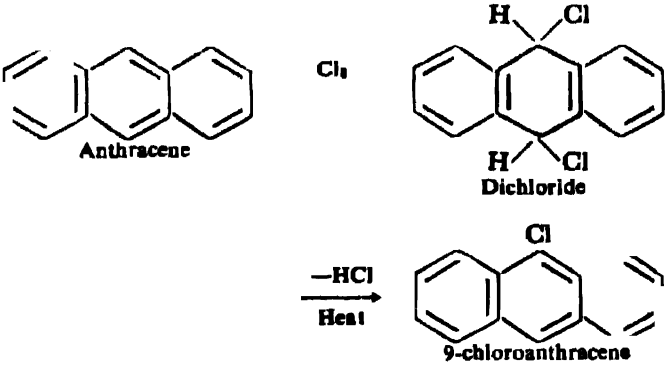


It undergoes electrophilic substitution. The carbocation initially formed is the most stable one, in which aromatic sextets are preserved in two of the three rings. The carbocation can then either give up a proton to yield the substitution product or accept a base to yield the addition product. The tendency of anthracene to undergo addition is due to the comparatively small sacrifice in resonance energy (=50·2 kJ mol^{-1}).

In the anthracene molecule the π-electron densities are unity at all positions. The self-polarisabilities of various nuclear positions are in the following order : 9 > 1 > 2. Consequently position 9 will be most reactive, then 1 and finally 2.

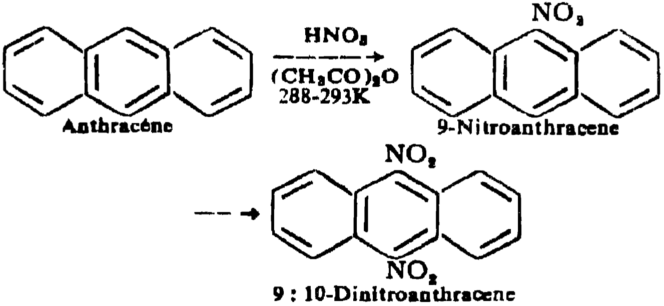
Its important chemical reactions are :

(*i*) ***Halogenation.*** On passing chlorine through a cold solution of anthracene in carbon disulphide, anthracene dichloride is produced. This loses a molecule of hydrogen chloride on heating or treatment with alkali and forms 9-chloroanthracene.



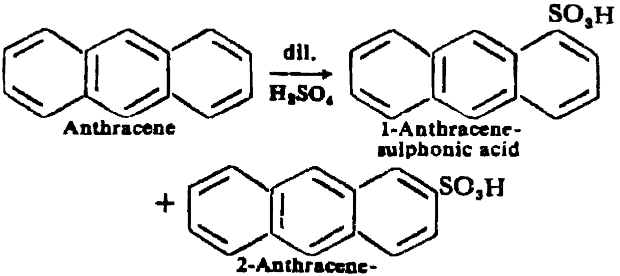
Chlorination of anthracene at 460K gives 9-chloroanthracene along with some 9 : 10-dichloroanthracene. Bromine reacts similarly.

(*ii*) *Nitration.* Aqueous nitric acid oxidises anthracene to anthraquinone. Nitration is, therefore, carried out in acetic anhydride at 288-293K when it gives 9-nitroanthracene and 9 : 10-dinitroanthracene.



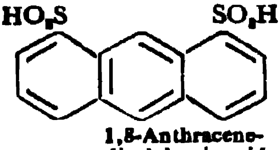
9 : 10-Dinitroanthracene

(*iii*) *Sulphonation.* Anthracene is readily sulphonated to form a mixture of 1- and 2-anthracenesulphonic acids. Some disulphonic acids are also produced. More of the 2-isomer is obtained at higher temperature.

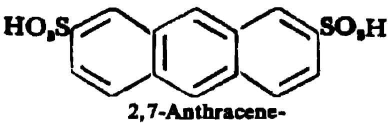


2-Anthracene-sulphonic acid

With excess of concentrated sulphuric acid 1 : 8-anthracenedisulphonic acid is obtained at low temperatures while 2 : 7-isomer is obtained at higher temperatures.

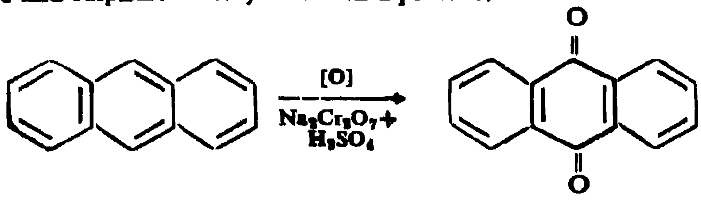


1,8-Anthracene-disulphonic acid
(*At low temp.*)



2,7-Anthracene-disulphonic acid
(*At higher temp.*)

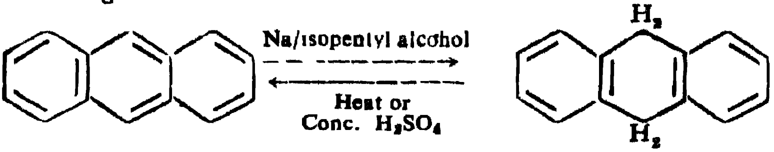
(*iv*) *Oxidation.* Anthracene on oxidation with sodium dichromate and sulphuric acid yields anthraquinone.



Anthracene

Anthraquinone

(v) *Reduction.* On reduction with sodium and *iso*pentanol, anthracene yields 9 : 10-dihydroanthracene which on heating or on treatment with concentrated sulphuric acid loses two hydrogen atoms to give back anthracene.



Anthracene 9, 10-dihydroanthracene

Catalytic reduction using nickel at 470-520K yields tetra-hexa-, octa- and finally *perhydroanthracene ($C_{14}H_{24}$) depending on the quantity of hydrogen used.

$$\underset{\text{Anthracene}}{C_{14}H_{10}} \xrightarrow[\text{Ni}]{H_2} \underset{\text{tetrahydroanthracene}}{C_{14}H_{14}} \xrightarrow{H_2} \underset{\text{hexahydroanthracene}}{C_{14}H_{16}} \xrightarrow{H_2} \underset{\text{octahydroanthracene}}{C_{14}H_{18}} \xrightarrow{H_2} \underset{\text{perhydroanthracene}}{C_{14}H_{24}}$$

5. **Uses of Anthracene.**—Anthracene is used in dyestuff industry for the manufacture of alizarin and anthraquinone dyes.

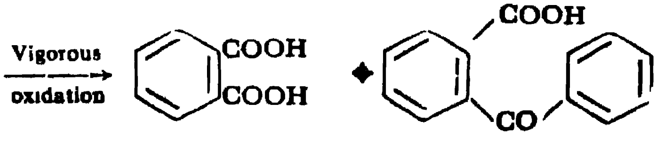
6. **Structure.**—(1) The molecular formula of anthracene as calculated from its analytical data is $C_{14}H_{10}$. The formula suggests that anthracene may be related to benzene and naphthalene.

$$\underset{\text{Benzene}}{C_6H_6} \xrightarrow{+4C\ ,\ +2H} \underset{\text{Naphthalene}}{C_{10}H_8} \xrightarrow{+4C\ ,\ +2H} \underset{\text{Anthracene}}{C_{14}H_{10}}$$

(2) Like benzene and naphthalene it gives addition and substitution reactions, *e.g.*, halogenation, sulphonation and nitration. This supports the view that anthracene is somehow related to benzene and naphthalene.

(3) Anthracene on bromination gives bromoanthracene, $C_{14}H_9Br$ which on fusion with solid caustic potash gives hydroxyanthracene, $C_{14}H_9OH$. The latter on vigorous oxidation forms phthalic acid and a small quantity of *o*-benzoylbenzoic acid.

$$\underset{\text{Anthracene}}{C_{14}H_{10}} \xrightarrow{Br_2} \underset{\text{Bromoanthracene}}{C_{14}H_9Br} \xrightarrow[\text{fuse}]{\text{KOH}} \underset{\text{Hydroxyanthracene}}{C_{14}H_9OH}$$



Phthalic acid *o*-Benzoylbenzoic acid

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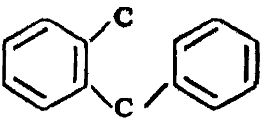
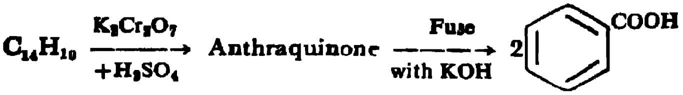
*The prefix *per* is often used to denote complete hydrogenation of a ring system.

This suggests the presence of at least two benzene rings in anthracene and that its skeleton is as shown in the margin.

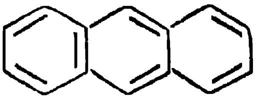


(4) Anthracene on oxidation with dichromate and sulphuric acid gives anthraquinone which on fusion with potassium hydroxide at 520K gives two molecules of benzoic acid.

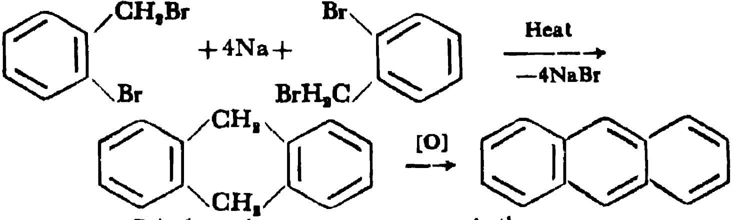


This confirms the presence of two benzene rings in anthracene.

(5) The skeleton of anthracene given above contains 14 carbon atoms. In order to fit 10 hydrogen atoms and retain the quadri-valency of each carbon atom, the middle ring must be closed. In other words, anthracene is made up of three benzene rings fused together in a linear manner as given in the margin.



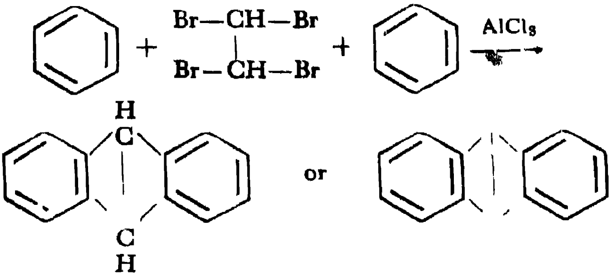
(6) This view is further confirmed by synthesis of anthracene by heating *o*-bromobenzyl bromide with sodium followed by mild oxidation of dihydroanthracene obtained in the first step.



Dihydroanthracene Anthracene

(7) *Position of double bonds in anthracene.*

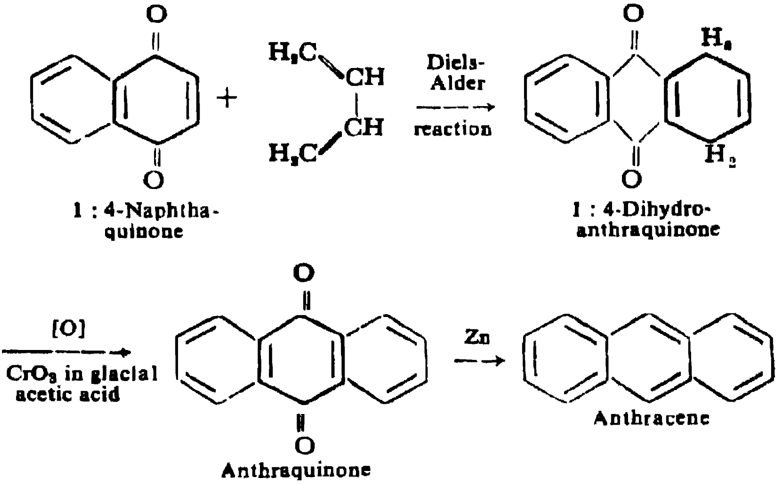
(*a*) Anthracene is synthesised by Friedel-Crafts condensation between benzene and acetylene tetrabromide.



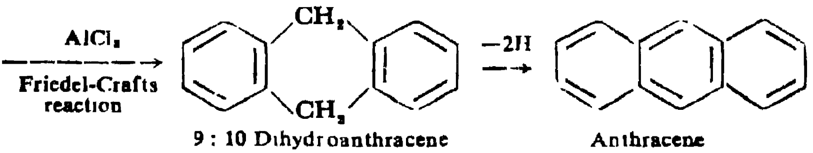
I Anthracene

This suggests formula I for anthracene having a *para*-bond. This structure, however, has been considered unlikely for the following reasons :

(*i*) Synthesis of anthracene from naphthaquinone or methylene bromide, etc., indicates the absence of a *para*-bond.

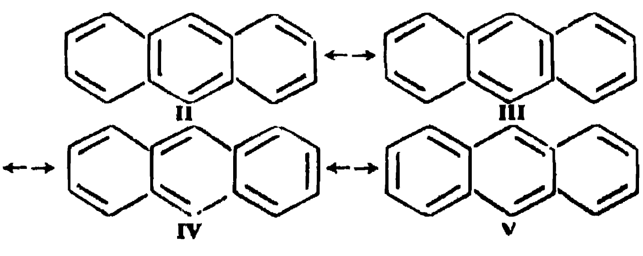


$2C_6H_6 + 2CH_2Br$.



(*ii*) X-ray analysis studies indicate that all the carbon atoms of anthracene lie in the same plane. The distance between the para carbon atoms in each ring has been shown to be the same as in benzene.

According to the modern view based on all available evidence anthracene is a resonance hybrid of the following four resonating structures (**II—V**).



The resonance energy of anthracene is 351·5 kJ mol^{-1}.

The C$_1$—C$_2$ bond is double in three out of four structures and has, therefore, ¾ double bond character. C$_2$—C$_3$ bond is double only in one and single in three structures. It has thus ¼ double bond character. Double bond character of other bonds can be calculated in a similar manner.

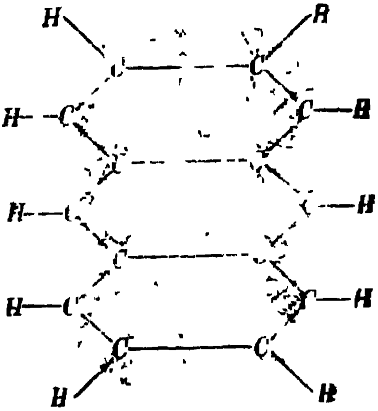


Fig. 2·1—π-clouds above and below the plane of rings in the anthracene molecule.

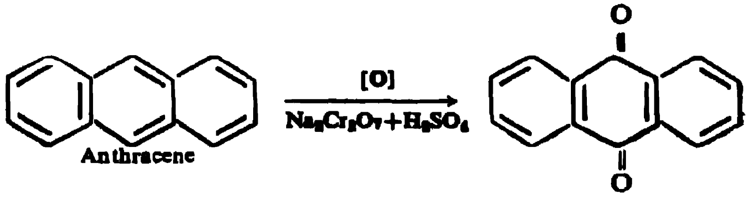
Consideration of atomic orbitals shows that fourteen carbon atoms lie at the corners of three fused hexagons. Each carbon atom is attached to three other atoms by σ bonds resulting from the overlapping of trigonal sp^2 orbitals and all carbon and hydrogen atoms lie in a single plane. There is a cloud of π electrons formed by the overlapping of p-orbitals above and below the plane of carbon atoms. The cloud may be considered as made up of three partially overlapping sextets (π clouds containing six electrons) which have two pairs of π-electrons in common

DERIVATIVES OF ANTHRACENE

7. **Anthraquinone.**—There are nine possible isomeric quinones of anthracene. Out of these 1 : 2-, 1 : 4- and 9 : 10- are known. The last one is the most important and is referred to simply as anthraquinone.

Preparation. Different methods used for the preparation of anthraquinone are :

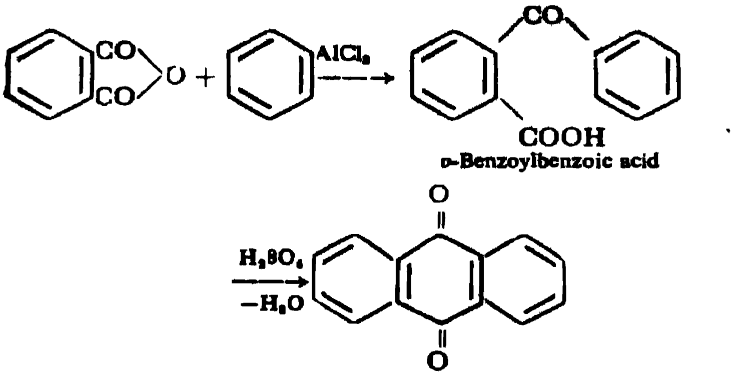
(*i*) *By oxidation of anthracene with sodium dichromate and sulphuric acid.* Before 1914, anthraquinone was prepared by oxidising anthracene with dichromate and sulphuric acid (yield =90%). Later on it was found cheaper to oxidise crude anthracene containing carbazole. During oxidation carbazole is completely oxidised whereas anthracene gives anthraquinone.



Anthracene

Anthraquinone

(*ii*) ***By heating phthalic anhydride with benzene in the presence of anhydrous aluminium chloride (Friedel-Crafts reaction).*** **This synthetic method (yield=90-95%) has proved to be the cheapest today.**



o-Benzoylbenzoic acid

Anthraquinone

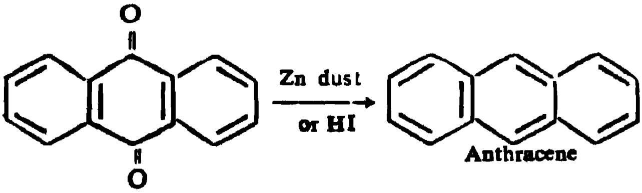
This synthesis of anthraquinone also proves its structure.

Properties. It gives pale-yellow, odourless, needle-shaped crystals (m.p. 541K) which sublime on heating. It is insoluble in water and alcohol but soluble in hot benzene or glacial acetic acid. It is very stable and shows very little resemblance to *p*-benzoquinone. For example, it is odourless, is not very volatile, and is not reduced by sulphurous acid.

Various chemical properties of anthraquinone are :

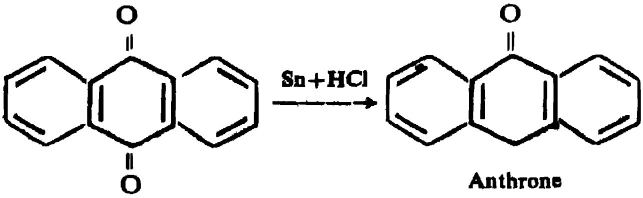
(1) *Reduction.* The nature of the reduction product depends on the reducing agent used. For example,

(*i*) When distilled with zinc dust or when heated with hydriodic acid at 420K, it forms anthracene.



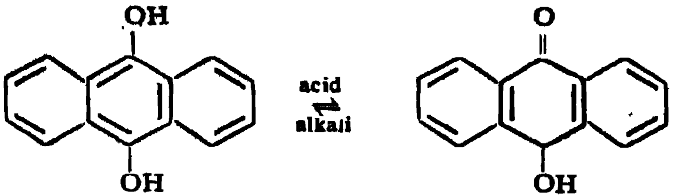
Anthracene

(*ii*) With tin and hydrochloric acid in acetic acid, it is reduced to anthrone. (10-keto-9,10 *dihydroanthracene*).



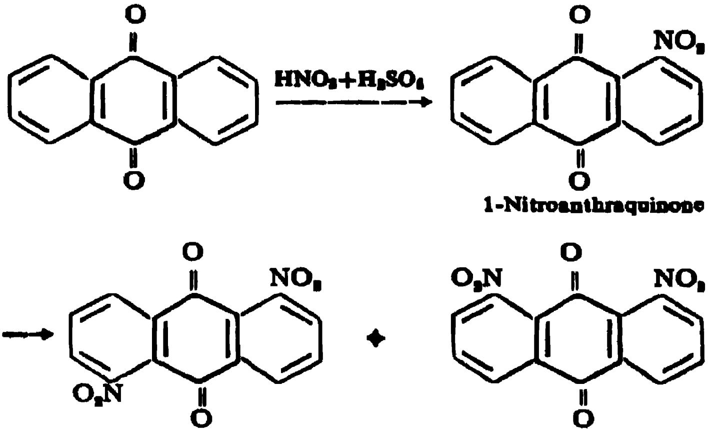
Anthrone

(*iii*) With zinc dust and aqueous sodium hydroxide anthraquinol (9, 10-anthracenediol or anthrahydroquinone) is produced. Anthraquinol on acidification, tautomerises to *oxanthranol*.



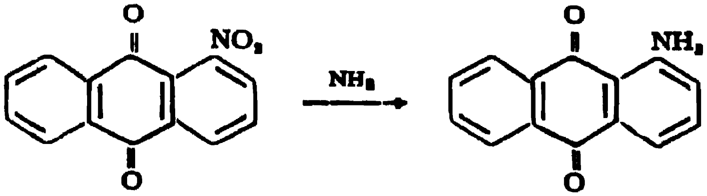
Anthraquinol Oxanthranol

(2) *Nitration*. On nitration with acid mixture it gives 1-nitroanthraquinone. On further nitration it gives mainly 1 : 5- and 1 : 8-dinitroanthraquinones with very small quantities of the 1 : 6- and 1 : 7- isomers.



1, 5-Dinitroanthraquinone 1, 8-Dinitroanthraquinone

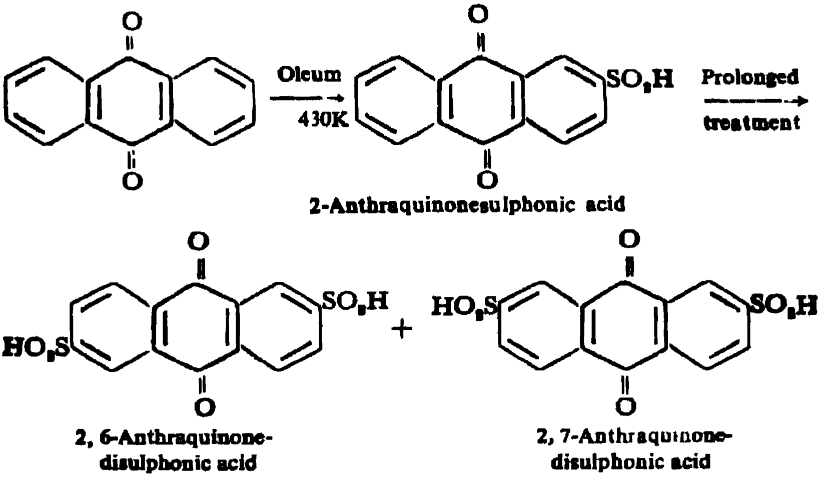
The nitro-group in the 1-position is very reactive and is replaced by an amino-group when 1-nitroanthraquinone is heated with ammonia.



1-Amino-anthraquinone

(3) *Sulphonation*. It is difficult to sulphonate anthraquinone with concentrated sulphuric acid. With oleum at 430K it gives mainly 2-sulphonic acid with small amount of 1-isomer.

Prolonged treatment gives 2 : 6- and 2 : 7-disulphonic acids in equal amounts.

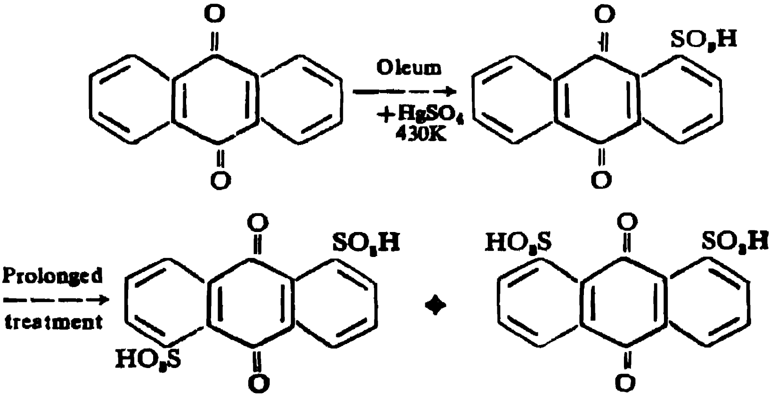


2-Anthraquinonesulphonic acid

2, 6-Anthraquinone-disulphonic acid

2, 7-Anthraquinone-disulphonic acid

In presence of mercuric sulphate (catalyst) 1-sulphonic acid is first produced. This gives 1 : 5- and 1 : 8-disulphonic acids on prolonged treatment.



1, 5-Anthraquinone-disulphonic acid

1, 8-Anthraquinone-disulphonic acid

The sulphonic acid group in 1- or 2-position is readily displaced, *e.g.*, by chlorine to give chloroanthraquinone.

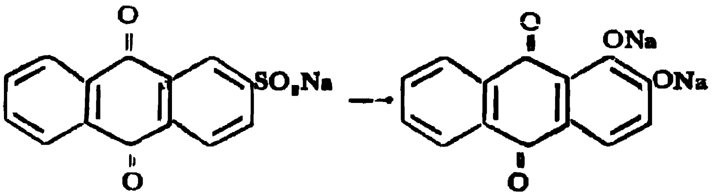
Anthraquinone is halogenated with great difficulty and does not give Friedel-Crafts reaction.

8. **Alizarin,** (1 : 2-*Dihydroxyanthraquinone*).—Alizarin is an important dyestuff. It is the chief constituent of madder root (मजीठ) wherein it is present as the glucoside, ruberythric acid. The dye derives its name from the Arabic *alizari* (=madder).

Preparation. Alizarin was originally obtained from madder root by hydrolysis of the glucoside present.

$$\underset{\text{Ruberythric acid}}{C_{26}H_{28}O_{14}} + 2H_2O \rightarrow \underset{\text{Glucose}}{2C_6H_{12}O_6} + \underset{\text{Alizarin}}{C_{14}H_6O_2(OH)_2}$$

At present it is manufactured synthetically by sulphonating anthraquinone (manufactured from phthalic anhydride—*see* page 2·672) with oleum at 430K and fusing the sodium salt of the product (2-sulphonic acid) with sodium hydroxide and the calculated quantity of potassium chlorate at 450—470K under pressure.



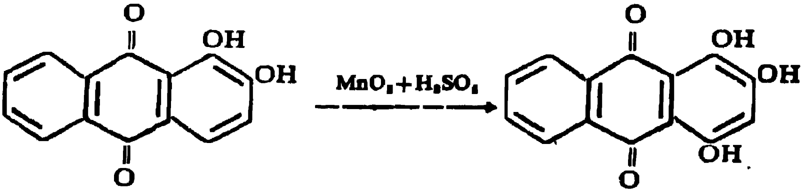
+ 3NaOH + [O]

Disodio deriv. of Alizarin

$+ Na_2SO_3 + 2H_2O$

Properties. Alizarin forms ruby-red crystals (m.p. 560K). It is insoluble in water and sparingly soluble in ethanol. It sublimes on heating and is, therefore, purified by sublimation. It dissolves in alkalis to give purple solutions of alizarates. Some important properties of alizarin are :

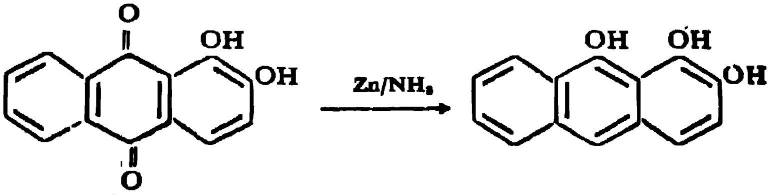
(*i*) On oxidation with MnO_2 and H_2SO_4 it gives purpurin—1, 2, 4-trihydroxyanthraquinone. Vigorous oxidation gives phthalic acid.



Alizarin

Purpurin

(*ii*) On reduction with zinc dust and ammonia it forms anthrarobin (dihydroxyanthranol)—a valuable medicine for skin diseases.



Alizarin

Anthrarobin

(*iii*) It is a mordant dye and the colour of the lake depends on the metal used. Aluminium gives a red lake (Turkey red). Ferric salts give a violet-black lake while chromium salts give a brown violet lake.

Aluminium and iron lakes are used for dyeing and printing cotton cloth. Aluminium and chromium lakes are used for dyeing wool.

Structure. (*i*) Molecular formula of alizarin as deduced from its analytical data and molecular weight determination is $C_{14}H_8O_4$.

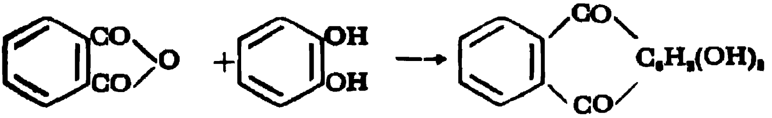
(*ii*) When distilled with zinc dust alizarin gives anthracene. This shows that *it is a derivative of anthracene.*

(*iii*) Anthraquinone on heating with a calculated quantity of bromine gives dibromoanthraquinone which on fusion with potassium hydroxide gives alizarin. This shows that *it is dihydroxyanthraquinone.*

(*iv*) Alizarin on vigorous oxidation yields phthalic acid. This shows that *the two hydroxyl groups are in the same ring*—the ring which is destroyed during oxidation, otherwise either hydroxy-phthalic acid would have been produced or the whole molecule would have been broken down completely.

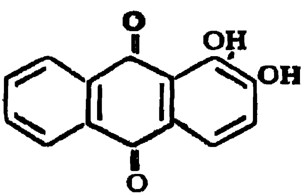
(*v*) The relative positions of the two —OH groups may be 1: 2-, 1 : 3-, 1 : 4 or 2 :3-.

(*vi*) Alizarin is obtained when phthalic anhydride is heated with 1, 2-benzendiol in the presence of a little concentrated sulphuric acid at 400K.

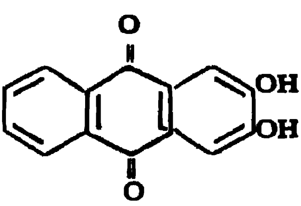


1, 2-benzenediol Alizarin

The two hydroxyl groups in alizarin must, therefore, be in the o-position, *i.e.*, 1 : 2- or 2 : 3-positions as shown in structure I and II given below :



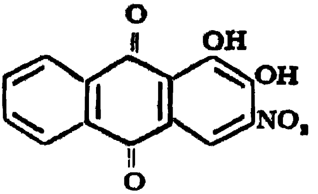
I



II

(*vii*) On nitration alizarin gives two isomeric mono-nitro derivatives, both of which on oxidation yield phthalic acid. This shows that nitro group is in the same ring which carries two hydroxyl groups.

Out of the two possible structures I and II for alizarin given above only the formula I admits the formation of two isomeric mono-nitro derivatives given below :



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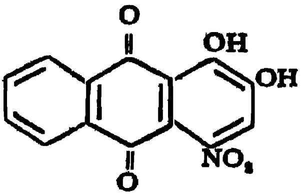
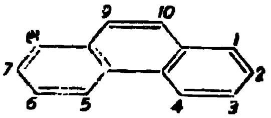


This shows that the formula I represents the correct structure of alizarin.

9. **Phenanthrene,** $C_{14}H_{10}$.—Phenanthrene is isomeric with anthracene. It occurs in coal-tar to the extent of 4 per cent. It is present along with anthracene in the Green-oil fraction of coal-tar. In the structural formula of phenanthrene, various carbon atoms are numbered as shown below :

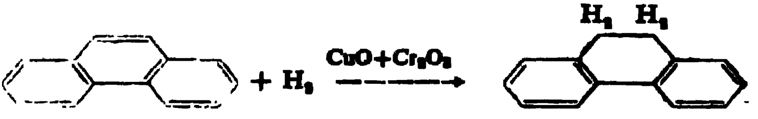


Isolation. Phenanthrene is isolated from the anthracene oil, a fraction of coal-tar collected between 540 and 630K. The solid cake obtained on cooling anthracene oil contains anthracene, phenanthrene and carbazole. This is powdered and phenanthrene present in it is extracted with solvent naphtha. The solution obtained on evaporation leaves phenanthrene.

Properties. It is a white solid (m.p. 372K) insoluble in water but soluble in alcohol, ether and benzene. Its solution in benzene shows a blue fluorescence.

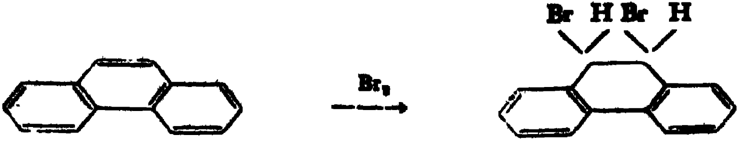
Chemically it behaves like other aromatic hydrocarbons and gives both addition and substitution products. It is very reactive in the 9 : 10-position. Some of its important properties are :

(*i*) ***Reduction.*** On catalytic reduction with H_2 (using CuO+Cr_2O_3 (as catalyst) it gives 9 : 10-dihydrophenanthrene.

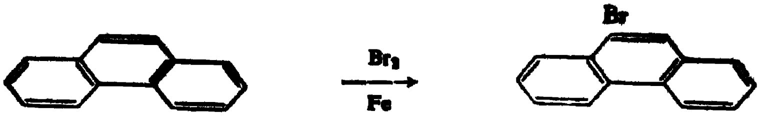


Phenanthrene 9 : 10-dihydrophenanthrene

(*ii*) ***Reaction with Bromine.*** It adds bromine to give 9 : 110, phenanthrene dibromide as easily as an ethylenic compound. When treated with bromine in presence of iron (halogen carrier) it gives 9-bromophenanthrene.



Phenanthrene Phenanthrene dibromide

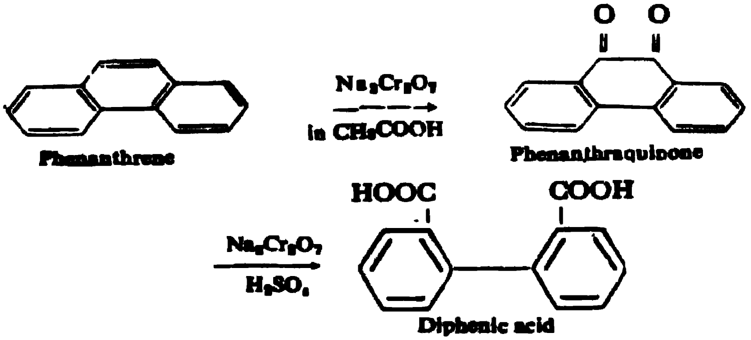


9-Bromophenanthrene

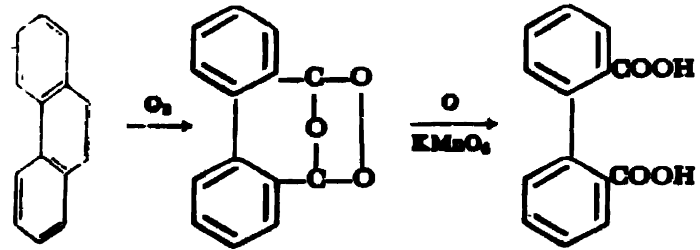
9-Bromophenanthrene is used in the preparation of other derivatives. For example,

$$\text{9-Bromo deriv.} \xrightarrow[\text{Heat}]{\text{CuCN}} \text{9-Cyano deriv.} \xrightarrow{H_2O} \text{9-Carboxylic acid}$$

(*iii*) *Oxidation*. On oxidation with dichromate in glacial acetic acid it gives phenanthraquinone which on further oxidation with dichromate and sulphuric acid gives diphenic acid.



(*iv*) *With ozone*. Phenanthrene gives a mono-ozonide which on oxidation gives diphenic acid.



(*v*) *Nitration*. On nitration it gives a mixture of three mono-nitro derivatives, the 3-isomer predominating.

(*vi*) *Sulphonation*. Phenanthrene on sulphonation gives a mixture of 1-, 2-, 3- and 9-phenanthrenesulphonic acids.

(*vii*) *Friedel-Crafts reaction*. Phenanthrene undergoes Friedel-Crafts reaction in 3-position mainly and in 2-position only to a small extent.

QUESTIONS

Essay Type :

1. Describe the isolation of anthracene from coal-tar. Discuss the structure of anthracene. How would you convert anthracene to anthraquinone and alizarin ? *(Marathwada B.Sc.1973)*

2. Discuss the evidence both analytical and synthetical on which the structure of anthracene is based.

3. Discuss the preparation, properties and constitution of alizarin. *(Delhi B.Sc 1972 ; Utkal 1976 ; Kerala 1973 ; Madras 1974)*

4. (*a*) Explain with reactions which positions in anthracene are more reactive. Why is it so ?

(*b*) How are the anthraquinone and anthrone prepared ?

5. Starting with naphthalene, describe the manufacture of an important dye.

6. Give important reactions of anthracene and phenanthrene.

Short Answer Type :

1. Give the mechanism of electrophilic substitution in anthracene.

2. Which is the most stable carbocation obtained from anthracene ?

3. What happens when anthracene undergoes (*i*) chlorination, (*ii*) nitration, (*iii*) sulphonation, (*iv*) oxidation and (*v*) reduction ?

4. How will you convert anthracene to alizarin ? *(Bangalore B.Sc. 1974)*

5. What happens when anthraquinone is (*i*) reduced, (*ii*) nitrated and (*iii*) sulphonated ?

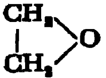
6. Indicating each step clearly, give a scheme of synthesis of phenantharene. *(Delhi B.Sc. Hons. 1978)*

7. Give explanation of the reactivity of 9 and 10-positions in anthracene nucleus. *(Delhi B.Sc. Hons. 1978)*

3

Heterocyclic Compounds—(i)

1. **Introductory.**—Heterocyclic compounds are cyclic compounds in which the ring includes in addition to carbon atoms one or more polyvalent atoms other than carbon (Greek, *Hetero*=other, different). These other elements are oxygen, nitrogen and sulphur. Some of the heterocyclic rings are readily opened and do not possess aromatic properties, *e.g.*, ethylene oxide, γ- and δ-lactones. These are not considered to be heterocyclic compounds.



Ethylene oxide

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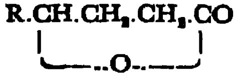
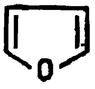
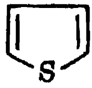


γ-Lactone

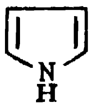
Heterocyclic compounds are those five- or six-member heterocyclic ring compounds which are stable and possess aromatic properties. Some common heterocyclic compounds containing five-member rings are furan, thiophene and pyrrole.



Furan

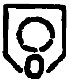


Thiophene

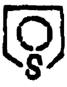


Pyrrole

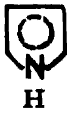
Each one of these behaves as a resonance hybrid of different structures. For convenience their hybrid structures are represented as given below :



Furan

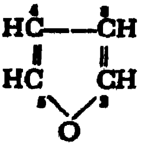


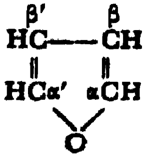
Thiophene



Pyrrole

2. **Furan, Oxacyclopenta-2,4-diene** (*furfuran*).—Furan derives its name from *furfur* (Latin = bran) because its aldehyde furfural is prepared by distilling bran with hydrochloric acid. It contains one oxygen atom in its ring. The positions of side-chains or substituents are indicated by Greek letters or numbers, number 1 being given to the oxygen atom.

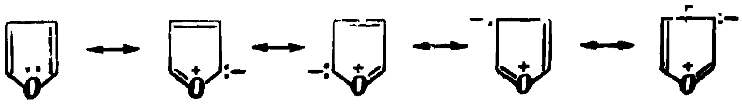




In all heterocyclic compounds containing one hetero-atom, number 1 is always given to the hetero-atom, i.e., numbering starts at the hetero atom always.

Thus there are two mono-substituted derivatives of furan, *viz*., 2 or α, and 3 or β. Similarly there are four disubstitution products, *viz*., 2 : 3 (α : β), 2 : 4 (α : β'), 2 : 5 (α ; α') and 3 : 4 (β : β').

Furan as a resonance hybrid. Furan behaves as a resonance hybrid of the following five resonating structures (I to V). It has a resonance energy of 71·1—96·2 kJ mol^{-1}. Since to be aromatic, a monocyclic molecule must be planar and have $(4n+2)$ π electrons. Out of the six electrons needed for the purpose two electrons are the lone pair of electrons of oxygen. As evaluated from its NMR data, furan is less aromatic than benzene.



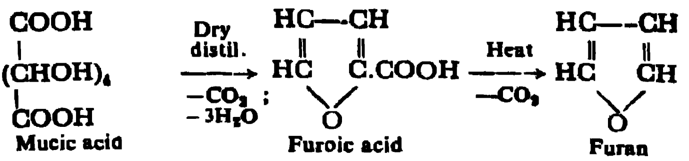
I II III IV V

(*Main contributing structures to the resonance hybrid*)

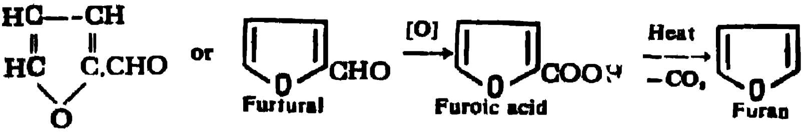
Canonical structures carrying no charge are more stable than those carrying unlike charges. Among the charged structures, the larger the charge separation, the less stable is the canonical structure. Accordingly II and III are more stable structures than IV and V. Hence, I, II and III are the main contributing structures to the resonance hybrid and consequently the resonance hybrid has a larger electron density at position 2 (or 5) than at 3 (or 4).

Preparation. (*i*) Furan is obtained by distillation of wood, especially pine-wood.

(*ii*) Dry distillation of mucic acid gives furoic acid which when heated at its b.p. yields furan.



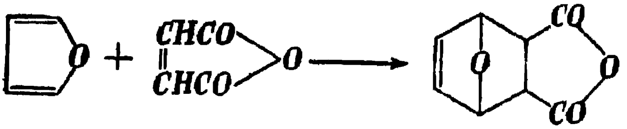
(*iii*) Furfural on oxidation gives furoic acid which on heating decarboxylates to give furan.



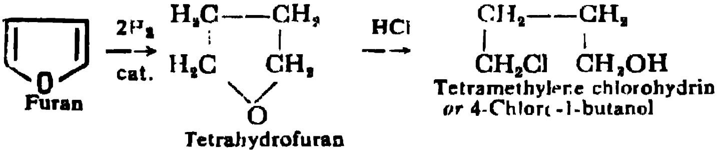
Properties. It is a colourless liquid (b.p. 305K), insoluble in water but soluble in alcohol and ether. It turns a pine splint moistened with hydrochloric acid, green (*Test*).

Chemically furan resembles benzene but tends to break open readily at the oxygen linkages. Some important reactions of furan are :

(1) **Diels-Alder reaction.** Furan is less aromatic than thiophene and pyrrole and is the only one of these which undergoes Diels-Alder reaction.

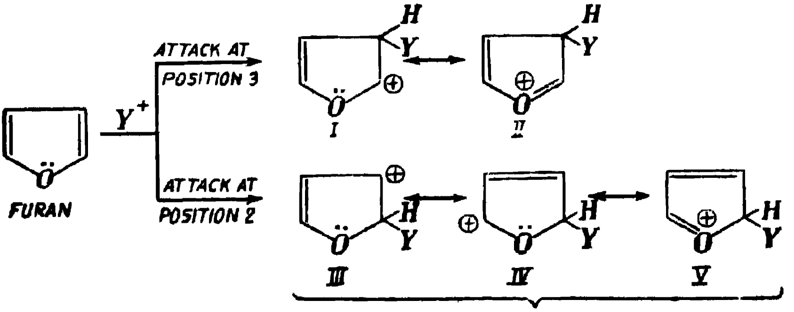


(2) **Reduction.** On catalytic reduction using Raney Ni or Pd-PdO catalyst, it forms tetrahydrofuran (THF—*an inert solvent*) which breaks open on treatment with hydrogen chloride to form tetramethylene chlorohydrin. With ammonia THF gives pyrrolidine.



(3) **Electrophilic Substitution Reactions.** As stated earlier furan is a resonance hybrid, having a larger electron density at position 2 (or 5) than at 3 (or 4). During electrophilic substitution the electrophile is expected to attack at position 2 (or 5), this being a centre of higher electron density. In practice 2-substitution is actually favoured.

Alternatively the controlling step in the electrophilic aromatic substitution is the attachment of electrophilic reagent to the aromatic ring in such a way as to yield the most stable carbocation. Let us apply this very approach to account for the reactions of furan.



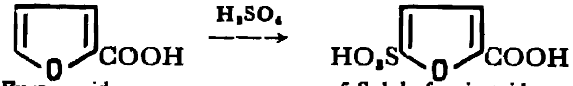
More stable carbocation being a hybrid of larger number of resonating structures resulting in greater spreading of charge.

Attack at position 3 gives a carbocation which is the resonance hybrid of two structures I and II. Attack at position 2 yields a resonance hybrid of three structures III, IV and V. The extra stabilization conferred on the latter hybrid by larger number of resonating structures resulting in greater spreading of charge makes this carbocation more stable.

Hence 2-substitution will be favoured, since it results in the formation of a more stable carbocation.

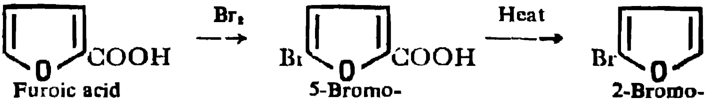
Furan ring is more reactive than benzene. This is because of the donation of the oxygen lone-pair as a result of which furan ring becomes activated. Thus furan undergoes substitution reactions more readily than does benzene. Substituents enter 2- or 5-position. If both of these positions are occupied, the substituent enters the 3-position.

(*i*) **Nitration and Sulphonation.** Furan is very readily attacked by concentrated acids and probably the oxonium salt is involved. Attempts at direct nitration (with acid mixture) and sulphonation results in the formation of resinified products. However, 2-Nitrofuran is obtained by nitrating it with acetyl nitrate. 2-Sulphonic acid may be prepared by treating furan with pyridine-sulphur trioxide. Sulphonation can, however, be carried out directly if a group with —I effect is present in the ring, *e.g.*, furoic acid can be directly sulphonated to 5-sulphofuroic acid.



Furoic acid 5-Sulphofuroic acid

(*ii*) **Halogenation.** Furan readily reacts with halogens but polymerisation is caused by the halogen acid liberated during the reaction. Because of this difficulty, halogeno-derivatives are obtained indirectly. For example furoic acid on bromination gives 5-bromofuroic acid which on decarboxylation yields 2-bromofuran.

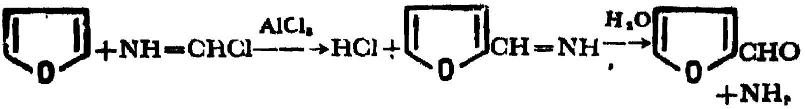


Furoic acid 5-Bromo-furoic acid 2-Bromo-furan

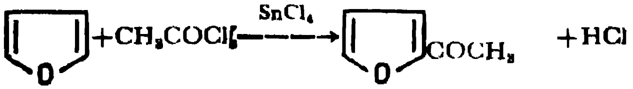
However, direct chlorination of furan has been found possible at 230K when it gives 2-chlorofuran and 2, 5-dichlorofuran as the main products.

(*iii*) **Gattermann reaction** Furan undergoes Gattermann reaction when treated with a mixture of hydrogen cyanide and hydrogen chloride in presence of aluminium chloride, followed by decomposition of the complex produced with water and furfural is obtained.

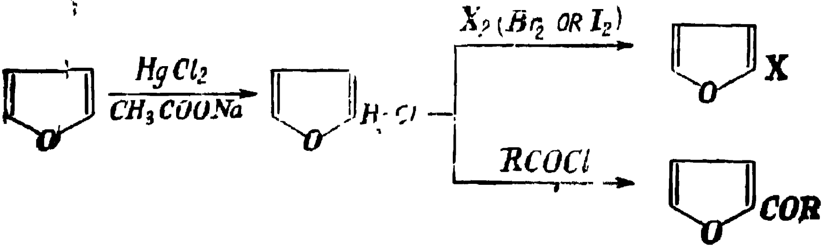
$$HCl + HCN \xrightarrow{AlCl_3} HN{=}CHCl$$



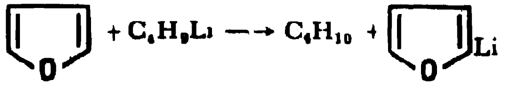
(iv) **Friedel-Crafts reactions.** Since aluminium chloride attacks the ring, stannic chloride is used in its place to carry on Friedel-Crafts reactions. Alkylation reactions with furan result in polymerisation and are, therefore, not possible. Acylation can, however, be brought about with acid chlorides or anhydrides using stannic chloride as catalyst. Boron trifluoride in ether (exists as complex $Et_2O^+—BF_3^-$) has proved to be a better catalyst in acylation with anhydrides.

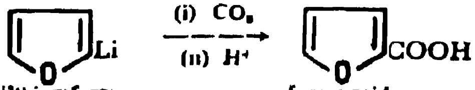


(v) **Mercuration.** When heated with mercuric chloride in acqueous sodium acetate, furan gives 2-chloromercurifuran. The mercuri-group can be readily replaced by bromine, iodine or an acyl group.



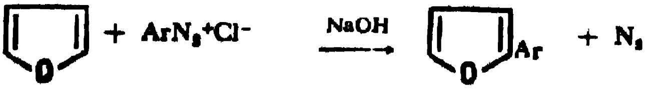
(vi) **Reaction with n-butyl-lithium.** Furan gives 2-lithiumfuran when treated with n-butyl-lithium. This gives the usual reactions of organo-lithium compounds, e.g., with carbon dioxide it gives furoic acid.





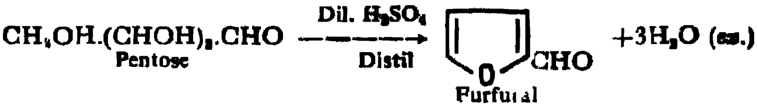
2-lithiumfuran furoic acid

(vii) **Gomberg reaction.** Furan on treatment with diazonium salts in alkaline solution, gives arylfuran (*Gomberg reaction*).



3. Furfural, 2-Furancarbaldehyde, or 2-Furaldehyde (*Oxacyclopenta-2, 4-diene-2-carbaldehyde*)

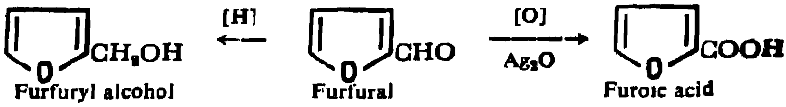
Preparation. (*i*) *By distilling a pentose with dilute sulphuric acid*



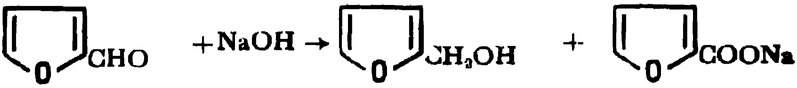
(*ii*) *By treating husk or bran (rich in pentoses) with dilute sulphuric acid followed by steam distillation (manufacture).*

Properties. It is a colourless oily liquid (b.p. 435K). Chemically it resembles benzaldehyde closely as shown by its various reactions given below :

(*i*) *Oxidation and Reduction* On oxidation with silver oxide furfural yields furoic acid while on reduction it yields furfuryl alcohol.



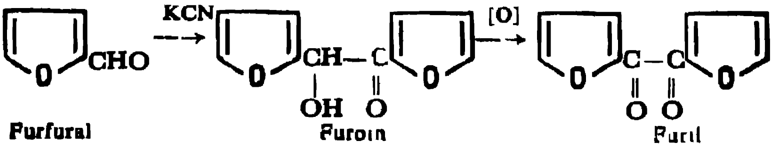
(*ii*) *Cannizzaro's reaction.* With aqueous sodium hydroxide it forms furfuryl alcohol and furoic acid.



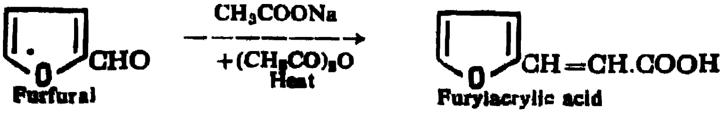
(*iii*) *With ammonia.* Furfural reacts with ammonia to form furfuramide, $(C_5H_4O)_3N_2$ (*cf.* C_6H_5CHO).

$$\underset{\text{Furfural}}{3C_5H_4O} + 2NH_3 \longrightarrow \underset{\text{Furfuramide}}{(C_5H_4O)_3N_2} + 3H_2O$$

(*iv*) *With alcoholic KCN*, furfural gives *furoin* which on oxidation gives *furil* (*cf.* benzoin condensation which on oxidation gives benzil).



(*v*) *Perkin's reaction.* It undergoes Perkin's reaction, *e.g.*, with sodium acetate and acetic anhydride it gives furylacrylic acid (*cf.* benzaldehyde).



(*vi*) *Claisen condensation.* Like benzaldehyde furfural undergoes Claisen condensation.

Tests. (*i*) It gives a red colour with aniline and hydrochloric acid.

(*ii*) It turns a pine splint moistened with hydrochloric acid green (*cf.* furan).

Uses. (*i*) In the preparation of dyes, plastics and maleic acid.

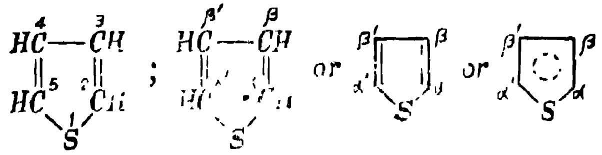
(*ii*) As solvent in the manufacture of synthetic rubber.

(*iii*) As an extraction liquid in petroleum refining

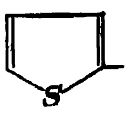
(*iv*) As a preservative for leather and wood.

(*v*) As a reagent in checking purity of ghee.

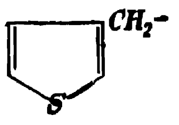
4. **Thiophene, Thiacyclopenta-2,4-diene, C_4H_4S**—Thiophene contains one sulphur atom in its ring. The positions of side-chains or substituents in thiophene are indicated by Greek letters or numbers as given below :



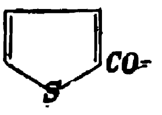
There is a close similarity between thiophene and benzene. For example, like benzene thiophene can be easily sulphonated, nitrated and chlorinated. This close similarity between the two has resulted in a similar nomenclature, *e.g.*,



2-thienyl
(*cf.* phenyl)



3-thenyl
(*cf.* benzyl)



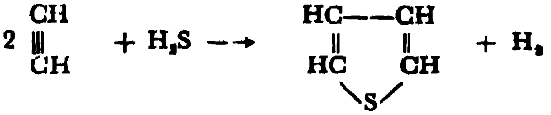
2-thenoyl
(*cf.* benzoyl)

Preparation. (*i*) ***From coal-tar.*** Benzene obtained from coal-tar contains thiophene. It is difficult to separate them by fractional distillation as their boiling points are very close to each other.

The mixture is shaken with cold concentrated sulphuric acid when thiophene gives thiophenesulphonic acid which is dissolved out in water. Thiophenesulphonic acid is treated with superheated steam to recover thiophene.

A better method of separation is by refluxing the mixture with aqueous mercuric acetate when thiophene is mercurated and benzene remains unaffected. Mercurated derivative is distilled with hydrochloric acid to recover thiophene.

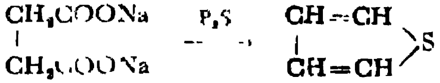
(*ii*) *Manufacture* Thiophene is manufactured by passing a mixture of acetylene and hydrogen sulphide through a tube containing Al_2O_3 at 670K.



It is also manufactured by reaction between *n*-butane and sulphur in vapour phase.

$$C_4H_{10}+4S \xrightarrow{920K} C_4H_4S+3H_2S$$

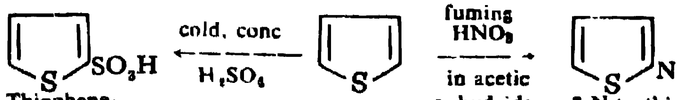
(*iii*) *Laboratory Method*. Thiophene may be prepared in the laboratory by heating sodium succinate with phosphorus trisulphide.



Properties. Thiophene is a colourless liquid (b.p 357K) smelling like benzene. It is insoluble in water but soluble in organic solvents. It does not show basic properties and is stable towards aqueous acids.

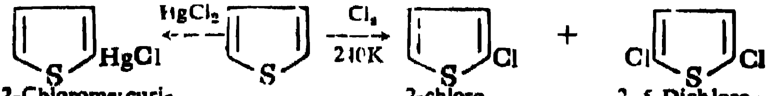
Chemically thiophene resembles benzene rather closely. As compared with furan and pyrrole, it is comparatively more stable. Its important reactions are :

(1) *Substitution reactions.* Like furan, thiophene undergoes electrophilic substitution. On the basis of charge distribution and stabilities of the carbocations, the electrophilic substitution would be expected to take place at position 2 (or 5). This is what actually occurs in practice. Nitration with fuming nitric acid in acetic anhydride gives 2-nitrothiophene. Sulphonation with cold concentrated sulphuric acid gives 2-sulphonic acid. Chlorination results in the formation of both substitution and addition products. However, at 240K, 2 chloro- and 2, 5-dichlorothiophene are the main products. On bromination with *N*-bromosuccinimide it gives 2-bromothiophene and 2-iodothiophene is obtained with iodine in presence of yellow mercuric oxide.



2-Thiophene-sulphonic acid

2-Nitrothiophene

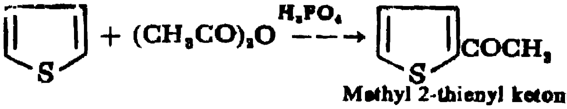


2-Chloromercuri-thiophene

2-chloro-thiophene

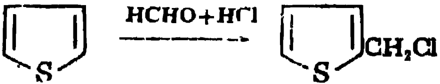
2, 5-Dichloro-thiophene

(2) *Friedel-Crafts reaction.* Like benzene, thiophene gives Friedel-Crafts reaction in presence of stannic chloride. For example, it is readily acylated in 2-position when treated with acid chloride in presence of $SnCl_4$ or better with acid anhydride in presence of phosphoric acid.



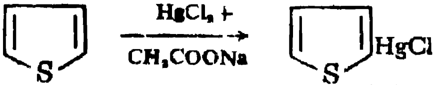
Methyl 2-thienyl ketone

(3) *Chloromethylation and Formylation.* Thiophene may be chloromethylated (with $HCHO+HCl$) and formylated (with dimethyl formamide and $POCl_3$) in 2-position.



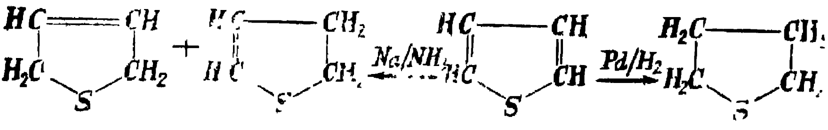
2-chloromethylthiophene

(4) *Mercuration.* On mercuration with mercuric chloride in the presence of sodium acetate (small amount), it gives 2-mercurichloride as the main product.



2-mercuri-chloride

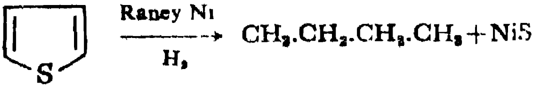
(5) *Reduction.* Catalytic hydrogenation of thiophene using large amount of the catalyst gives tetrahydrothiophene (thiophan). On reduction with sodium in liquid ammonia it gives 2 : 3- and 2 : 5-dihydrothiophene.



2 : 5- 2 : 3- dihydrothiophene

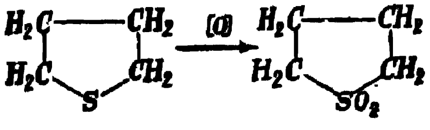
tetrahydrothiophene (*thiophan, thiolan*)

Catalytic reduction of thiophene with Raney nickel as catalyst gives *n*-butane as the main product, *i.e.*, it results in the removal of sulphur.



(6) *Thiophene does not behave like thioethers.* It does not from sulphonium salts and cannot be oxidised to sulphoxide or

sulphone. Tetrahydrothiophene on the other hand behaves like true thioether and is oxidised to sulphone.



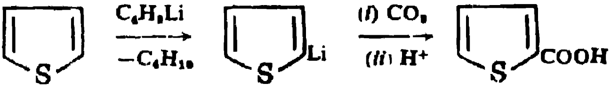
Thiophane
(A true thioether)

Sulphone

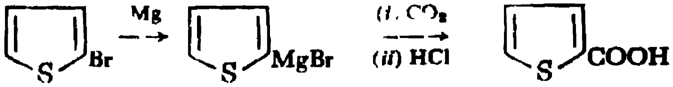
This shows that thiophene which has alternate double and single bonds is aromatic in character. This aromatic character vanishes with the disappearance of these double bonds in thiophan.

Oxidation with hydrogen peroxide, however, results in the opening of thiophene ring with oxidation of sulphur to sulphuric acid.

(7) *Formation of Lithium derivative.* Thiophene on treatment with *n*-butyl-lithium in ether, gives 2-lithiumthiophene. It is useful in the synthesis of various 2-substituted thiophenes.



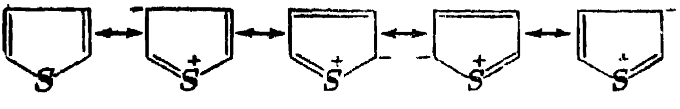
Various derivatives of thiophene may be obtained from the monobromo-derivatives. For example,



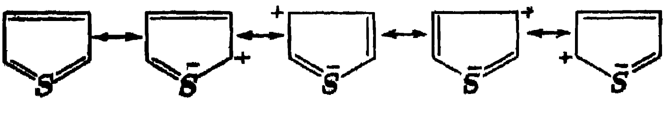
(8) *Indophenin reaction.* On treatment with isatin and sulphuric acid, thiophen gives a blue colour (*Test*).

Thiophene as a resonance hybrid. Thiophene behaves as a resonance hybrid and its resonance energy is 117—130 kJ mol^{-1}. Like oxygen atom in furan, sulphur atom in thiophene contributes two electrons to form a $(4n+2)$ π-electron molecule. In comparison to oxygen and nitrogen atoms sulphur is less electronegative and it can also use $3d$-orbitals. On account of these facts more canonical forms are possible for thiophene than for furan or pyrrole. In the canonical forms of thiophene given below, in group (*a*) structures, the sulphur atom uses *p*-orbitals whereas in group (*b*) structures it makes use of its *d*-orbitals also.

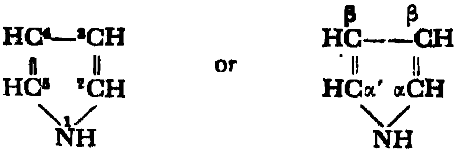
(*a*)



(*b*)



5. Pyrrole, Azacyclypenta-2,4-diene C_4H_5N.—Pyrrole is an important heterocyclic compound having a five-member ring containing a nitrogen atom. Various atoms of the ring are numbered as follows :

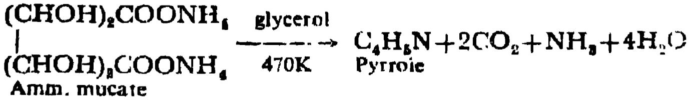


It occurs in coal-tar and bone oil.

Preparation. (*i*) *Isolation from bone oil.* Bone oil is washed with dilute alkali to remove acidic substances and then with acid to remove strongly basic substances (pyridine bases) and finally fractionated. Pyrrole distils over in the fraction boiling between 370 and 420K. This is fused with potassium hydroxide. Solid potassiopyrrole is formed which on steam-distillation yields pure pyrrole.

$$\underset{\text{Potassio-pyrrole}}{C_4H_4NK}+H_2O \xrightarrow[\text{distillation}]{\text{steam}} \underset{\text{Pyrrole}}{C_4H_4NH}+KOH$$

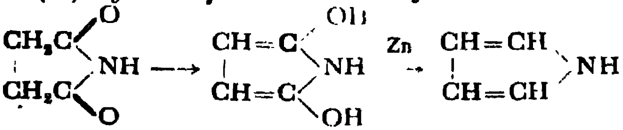
(*ii*) *By distilling a mixture of ammonium mucate and glycerol at 470K.*



$$\begin{array}{l}(CHOH)_2COONH_4\\ |\\ (CHOH)_2COONH_4\end{array} \xrightarrow[470K]{\text{glycerol}} \underset{\text{Pyrrole}}{C_4H_5N}+2CO_2+NH_3+4H_2O$$

Amm. mucate

(*iii*) *Pyrrole is formed on distilling succinimide with zinc dust.*

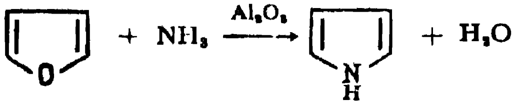


Succinimide (keto form) Enol form Pyrrole

(*iv*) *It may be synthesised by passing acetylene mixed with ammonia through a red-hot tube.*

$$2C_2H_2+NH_3 \rightarrow C_4H_5N+H_2$$

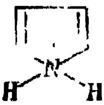
(*v*) *Manufacture.* Pyrrole can be manufactured by passing a mixture of furan, ammonia and steam over heated alumina (*catalyst*).

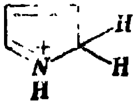


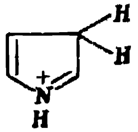
Properties. It is a colourless liquid (b.p. 404K) sparingly soluble in water but readily soluble in alcohol and ether. It rapidly darkens on exposure to air and finally forms a resinous mass. Vapours of pyrrole turn a pine splint moistened with hydrochloric acid red. Pyrrole derives its name from this characteristic reaction (Greek : *Pyrros*=fiery red ; Latin : *Oleum*=oil).

Chemically it shows the reactions of aromatic compounds. It is less aromatic than thiophene but more aromatic than furan. Some important reactions of pyrrole are :

(*i*) *Basic nature.* Nirogen atom in pyrrole contributes its lone pair of electrons to form a $(4n+2)$ π-electron molecule. Because of this contribution, the availability of the lone pair of electrons of the nitrogen atom for protonation is very much decreased. As a result of this pyrrole is a very weak base (*cf.* aniline). However, in acid solution, protonation also occurs at the 2- and 3-positions, and in concentrated solution pyrrole polymerises (to form pyrrole-red).



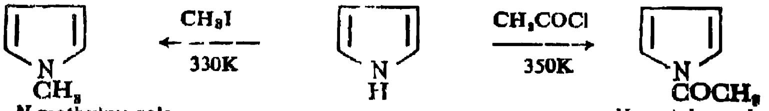




(*ii*) *Replacement of imino-hydrogen* The imino-hydrogen of pyrrole is replaced by sodium, potassium, alkyl or acyl radicals. For example, on heating it with solid caustic potash, potassiopyrrole is formed.

$$C_4H_4NH + KOH \rightarrow C_4H_4N^-K^+ + H_2O$$

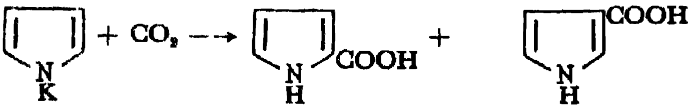
It reacts with acetyl chloride at about 350K to give *N*-acetylpyrrole With methyl iodide at 330K it forms *N*-methylpyrrole.



N-methylpyrrole *N*-acetylpyrrole

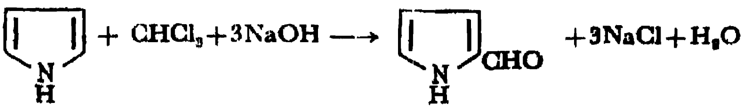
These reactions when carried out at higher temperatures (420-490K) give the 2- or 3-substituted products in place of the *N*-compound. This is probably due to the rearrangement of the *N*-compound first formed.

(*iii*) *Resemblance with Phenols.* Potassiopyrrole reacts with carbon dioxide to form 2- and 3-pyrrolecarboxylic acid (*cf.* Kolbe-Schmitt reaction).



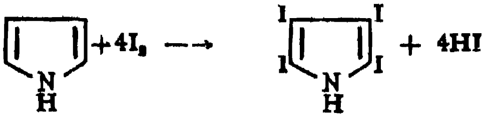
2-Pyrrolecarboxylic acid 3-Pyrrolecarboxylic acid

Pyrrole reacts with chloroform to yield Pyrrolecarbaldehyde (*cf.* Reimer-Tiemann reaction).



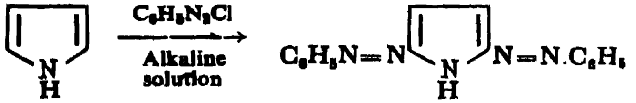
2-Pyrrolecarbaldehyde

(*iv*) *Halogenation*. It is easily halogenated. For example, with iodine solution it gives tetraiodo-pyrrole (*iodole*) used as a substitute for iodoform.



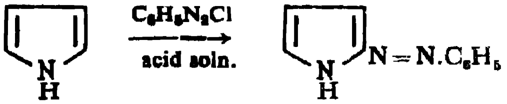
Iodole

(*v*) *Coupling*. Like phenol, pyrrole couples with diazonium salts in the 2-position in weakly acid solution. In alkaline solution coupling takes place in 2- and 5- positions to give bisazo-compound.



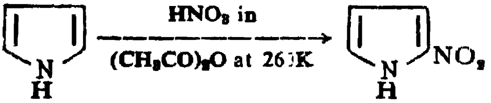
Pyrrole

Bisazo-compound



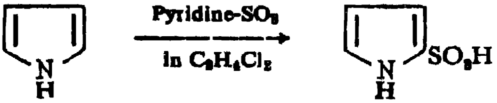
Coupling takes place in the 3-position if the 2- and 5-positions are not free.

(*vi*) *Nitration*. With nitric acid in acetic anhydride at 263K pyrrole gives 2-nitropyrrole.



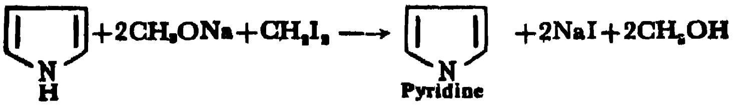
2-nitropyrrole

(*vii*) *Sulphonation*. With pyridine-sulphur trioxide in ethylene chloride, pyrrole is sulphonated to give the 2-sulphonic acid.



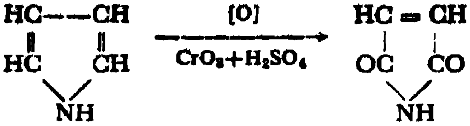
2-Pyrrolesulphonic acid

(*viii*) *Ring expansion*. When treated with sodium methoxide and methylene iodide pyrrole gives pyridine (six-member ring).



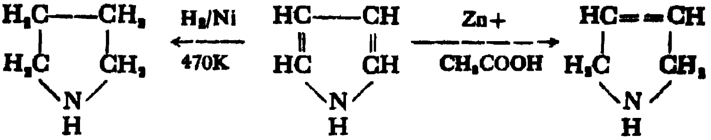
Pyridine

(*ix*) *Oxidation*. When oxidised with chromium trioxide in sulphuric acid pyrrole gives maleicimide.



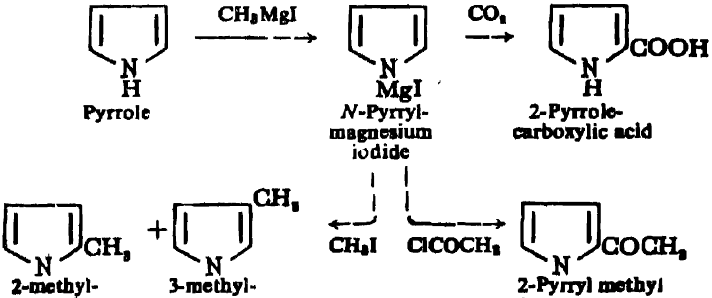
Maleicimide

(x) *Reduction.* Pyrrole on reduction with zinc and acetic acid gives pyrroline (2 : 5-dihydropyrrole). With nickel at 470K (catalytic reduction) pyrrole gives pyrrolidine (tetrahydropyrrole).



Pyrrolidine Pyrrole Pyrroline

(xi) *Reaction with Grignard reagent.* When pyrrole is treated with methylmagnesium iodide *N*-pyrrylmagnesium iodide is formed. This behaves as if the magnesium were combined at the 2- position since it yields 2-substituted pyrroles.



Pyrrole

N-Pyrrylmagnesium iodide

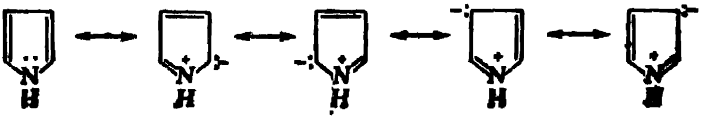
2-Pyrrolecarboxylic acid

2-methylpyrrole

3-methylpyrrole

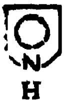
2-Pyrryl methyl ketone

Pyrrole as a resonance hybrid. Pyrrole behaves as a resonance hybrid of the following five resonating structures (I to V) but the main contributing structures are I, II and III. Its resonance energy is $87{\cdot}8-130$ kJ mol^{-1}.



I II III IV V

For convenience the hybrid structure is represented as given below and means a hybrid of structures I to V.



In the orbital picture of pyrrole, each atom of the ring (C or N) is held by σ bonds to three other atoms. These bonds result from the overlap of three sp^2 hybrid orbitals of each atom lying in a plane and inclined at 120°. There is one *p*-electron left with each carbon atom and two *p* electrons with the nitrogen atom. Overlap of these *p*-orbitals gives rise to π electron clouds (one above and one below the plane of the ring) which contain a total of six electrons, the *aromatic sextet*.

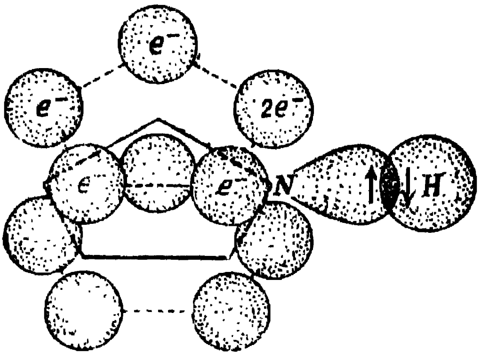
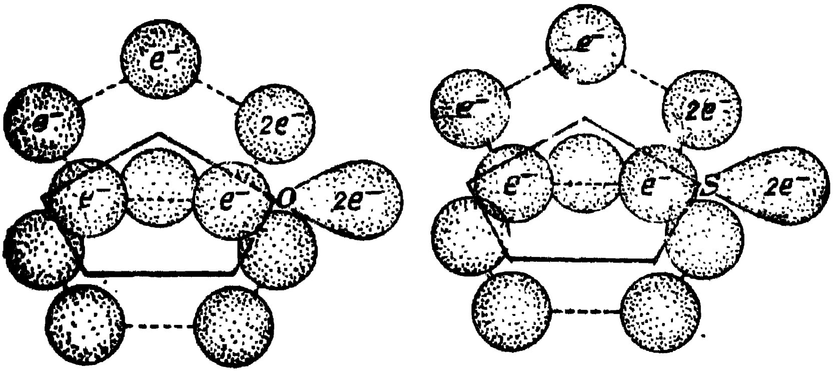


Fig. 47·1—Orbital structure of pyrrole with electron clouds above and below the plane of the pyrrole ring.

Stability of the pyrrole ring is due to delocalization of the π electrons. The stability of the ring is reflected by its abnormally low heat of combustion and its capacity to undergo substitution reactions.

Furan and thiophene resemble pyrrole in structure. Oxygen atom in furan and sulphur atom in thiophene are both sp^2 hybridized. In both the hetero atom donates two electrons to the aromatic sextet and carries an unshared pair of electrons in an sp^2 orbital.

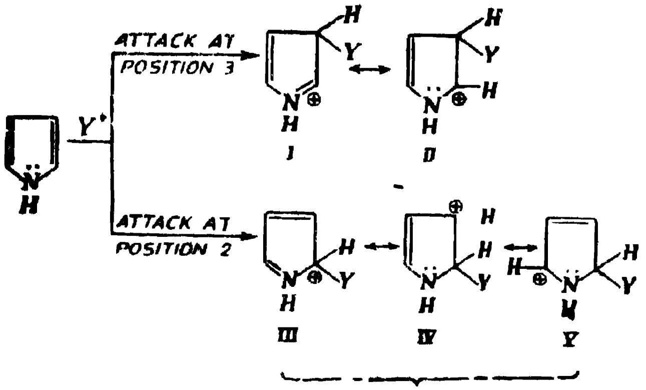


(*a*) (*b*)

Fig. 47·2—The orbital structures of (*a*) furan and (*b*) thiophene.

Orientation of Substitution Reactions in Pyrrole. In our study of electrophilic aromatic substitution we could account for orientation on the following basis : the controlling step is the attachment of the electrophilic reagent to the aromatic ring which takes place in such a way as to yield the most stable intermediate carbocation. Let us apply this very approach to account for the reactions of pyrrole.

Attack at position 3 gives a carbocation which is a resonance hybrid of structures I and II Attack at position 2 yields a resonance hybrid of structures III, IV (which are analogous to I and II) and V. The extra stabilization conferred on the latter hybrid by V makes his carbocation more stable.



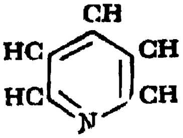
More stable carbocation

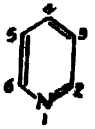
In a different explanation, attack at position 2 is faster because the developing positive charge is accommodated by three atoms of the ring instead of by only two.

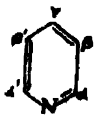
Compared to benzene, pyrrole is highly reactive because of contribution by the relatively stable structure III in which every atom has an octet of electrons. Nitrogen accommodates the positive charge. Resemblance of pyrrole with aniline in reactivity is due to the ability of nitrogen to share four pairs of electrons.

Orientations of substitution in furan and thiophene as well as their high reactivity can be accounted for in a similar way.

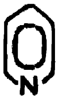
6. **Pyridine, Azabenzene, C_6H_5N**—Pyridine is an important heterocyclic compound containing a six-member ring. It may be regarded as benzene in which one $=CH-$ group has been replaced by $=N-$ The positions of side-chains are indicated by numbers or Greek letters.







Pyridine is a resonance hybrid of two Kekule structures and three charged structures given on page 3·64. For convenience its hybrid structure is represented as given below :



Pyridine occurs in the light oil fraction of coal-tar and in bone oil. It is a decomposition product of several alkaloids.

Isolation of Pyridine from Coal-tar. Light oil fraction of coal-tar is treated with dilute sulphuric acid. This dissolves pyridine and other basic substances which form soluble sulphates. The acid layer is treated with sodium hydroxide when the bases are liberated. These are purified by rectification. The mixture of pyridine bases so obtained is used industrially in denaturing spirits, and as a solvent in the purification of crude anthracene. Pyridine can be separated from this mixture of pyridine bases by repeated fractional distillation.

Properties. *Physical.* Pyridine is a colourless refractive liquid (b.p. 398K) having an unpleasant odour. It is miscible with water in all proportions and is hygroscopic. It is a good solvent for most organic compounds and dissolves many inorganic salts.

Chemical. Pyridine is basic in nature and resembles benzene in many of its properties. It is, however, less reactive and is only very slowly attacked by boiling nitric acid or chromic acid. Important reactions of pyridine are :

(1) **Basic nature.** It is a strong tertiary base which gives salts with inorganic acids and forms quaternary salts when heated with alkyl halides. These reactions involve nitrogen directly and are due to its unshared pair of electrons.

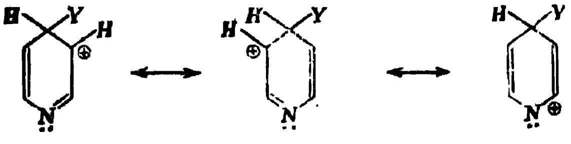
$$\begin{array}{cccc} C_5H_5\overset{+}{N}.CH_3\}I^- & \xleftarrow[\text{Heat}]{CH_3I} C_5H_5N & \xrightarrow{HCl} & C_5H_5\overset{+}{N}H\}Cl^- \\ \text{Pyridine methiodide} & \text{Pyridine} & & \text{Pyridine hydro-} \\ \text{or } N\text{-methylpyri-} & & & \text{chloride or} \\ \text{dinium iodide} & & & \text{Pyridinium chloride} \end{array}$$

The quaternary compound on heating to 570K forms 2- and 4-methylpyridines. On treatment with moist silver oxide it gives *N*-alkylpyridinium hydroxide, a strong base.

$$\begin{array}{ccc} C_5H_5\overset{+}{N}.CH_3\}I & \xrightarrow{AgOH} & C_5H_5\overset{+}{N}.CH_3\}OH^- \\ N\text{-methylpyri-} & & N\text{-methylpyri-} \\ \text{dinium iodide} & & \text{dinium hydroxide} \\ & & (\textit{a strong base}) \end{array}$$

(2) **Electrophilic substitution in pyridine.** It gives electrophilic substitution reactions and resembles a highly deactivated benzene derivative. It undergoes nitration, sulphonation and halogenation only under very vigorous conditions and does not undergo Friedel-Crafts reaction at all. Substitution occurs chiefly at 3- (or β) position.

Let us try to account for the reactivity and orientation on the basis of the stability of the intermediate carbocation (σ-complex). Attack at the 4-position yields a carbocation which is a resonance hybrid of structures I, II and III.

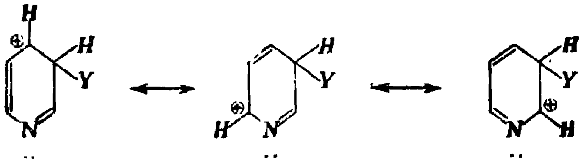


I II III

Electrophilic attack at 4-position

Especially unstable nitrogen has sextet only

Attack at 3-position yields a carbocation that is a resonance hybrid of structures IV, V and VI.



IV V VI

Electrophilic attack at 3-position

(Attack at the 2-position resembles attack at the 4-position just as the ortho attack resembles the para attack in benzene ring.)

Thus we find that an attack at 3-position yields a carbocation which is a resonance hybrid of three stable structures. Attack at 2- or 4-position yields a carbocation which is a resonance hybrid of only two stable structures.

The former being more stable, substitution occurs chiefly at 3- (or β-) position.

All these structures are less stable than the corresponding ones for attack on benzene because of electron withdrawal by the nitrogen atom. As a result of it, substitution in pyridine is slower than in benzene.

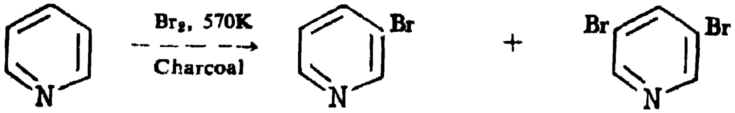
Out of the above structures, III is especially unstable since in it the electronegative nitrogen has only a sextet of electrons. As a result, attack at the 4-position (or 2-position) is especially slow and substitution occurs predominantly in 3-position

Some important electrophilic substitution reactions are :

(1) **Halogenation.** Pyridine undergoes halogenation just as benzene but less easily.

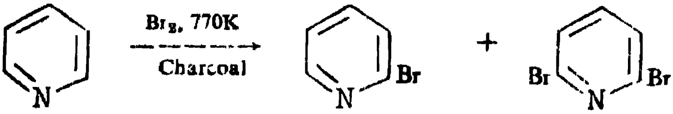
(i) *At ordinary temperatures* addition occurs to form dihalides, *e.g.*, $C_5H_5\overset{+}{N}Br$ Br^-, 1-bromopyridinium bromide.

(*ii*) *At 670K in presence of catalyst (pumice or charcoal)* it forms a mixture of 3 bromopyridine and 3, 5-dibromopyridine (or corresponding chloro-derivatives).



Pyridine 3-Bromopyridine 3, 5-Dibromopyridine

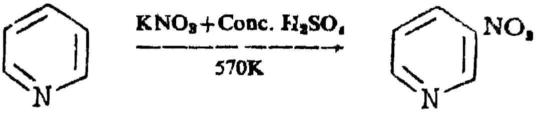
(*iii*) *At 770K in presence of catalyst,* it gives 2- bromo and 6- dibromo-derivatives.



Pyridine 2-Bromopyridine 2, 6-Dibromopyridine

Halogen atom in 2- or 4-position is reactive and readily replaced by OH, CN, NH_2 etc. (*cf.*, *o*- and *p*-chloronitrobenzene).

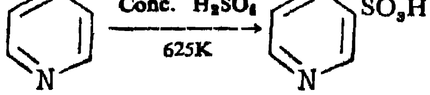
(2) **Nitration**. On heating with conc. H_2SO_4 and KNO_3 at 570K, it gives 3-nitropyridine



3-Nitropyridine

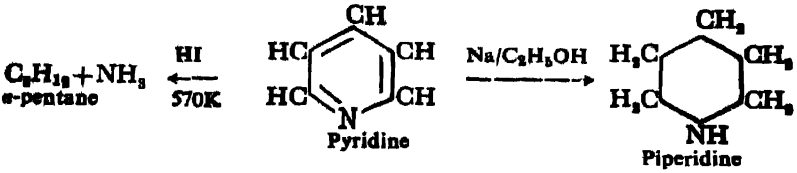
Pyridine reacts with concentrated nitric acid readily only when an OH or NH_2 group is present in the ring.

(3) **Sulphonation**. Sulphonation of pyridine is difficult. On heating with concentrated sulphuric acid at 6[illegible]0K for some hours, it gives 3-pyridinesulphonic acid.

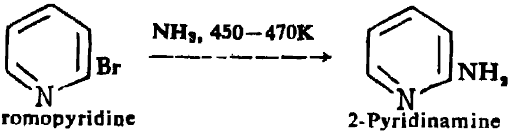


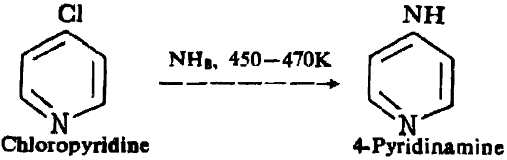
Pyridine 3-Pyridinesulphonic acid

(4) **Reduction**. Pyridine on reduction with sodium and ethanol gives piperidine. Electrolytic reduction or catalytic reduction using nickel also gives piperidine. On heating with hydriodic acid at 570K, the reduction is accompanied by ring fission to form *n*-pentane and ammonia.

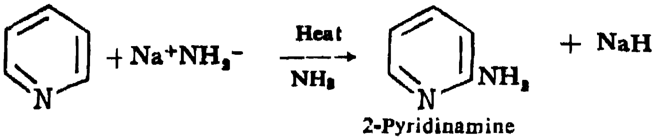


(5) **Nucleophilic substitution in pyridine.** Pyridine ring resembles a benzene ring that contains strongly electron-withdrawing groups. Nucleophilic substitution takes place readily, particularly at the 2- and 4-positions. For example, a halogen atom at the 2- and 4-positions is readily replaced by OH, CN, NH_2, etc.

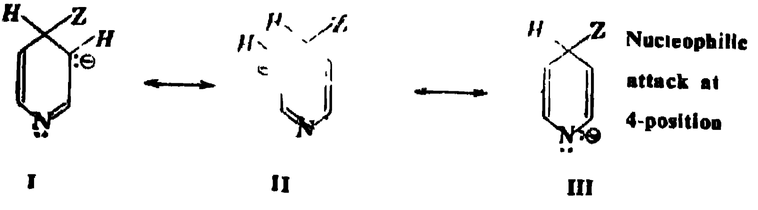




An important example of nucleophilic substitution is its amination by sodamide (**Chichibabin reaction**).



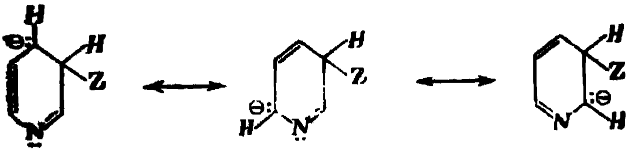
Nucleophilic attack at 4-position yields a carbanion which is a resonance hybrid of structures I, II and III.



Especially stable negative charge on nitrogen

(Attack at the 2-position is similar to attack at 4-position.)

Attack at the 3-position yields a carbanion, which is a resonance hybrid of structures IV, V and VI.



IV V VI

Nucleophilic attack at 3-position

Substitution at 2- or 4-position is favoured since it results in the formation of a stable carbanion.

All these structures are more stable as compared to the corresponding benzene derivatives on account of the electron-withdrawing nature of the nitrogen atom. Structure III is especially stable since the negative charge is located on the electronegative nitrogen atom which can accommodate it the best. Stability of these structures accounts for the nucleophilic substitution being more rapid in pyridine ring than in the benzene ring. Structure III being especially stable it is reasonable that nuleophilic substitution occurs more rapidly at the 2- and 4-positions than at the 3-position.

Thus we find the electron-withdrawing nature of nitrogen that makes pyridine unreactive towards electrophilic substitution, makes it highly reactive towards nucleophilic substitution.

Uses. Due to its strong basic property and solvent properties pyridine finds great use in organic chemistry. It is used :

(1) In reactions wherein a halogen acid is produced or where a molecule of halogen acid is to be removed to get unsaturated compounds, *e.g.*, in acetylation, benzoylation or removal of HBr from bromo-succinic ester (alc. KOH cannot be used as it would saponify the ester).

(2) As catalyst in many reactions, *e.g.*, in the formation of a Grignard reagent, in Perkin and Knoevenagel reactions.

(3) As solvent.

(4) In the manufacture of derivatives like vitamin B_6 and sulpha-pyridine (specific for pneumonia).

(5) In denaturing alcohol and for exterminating plant pests.

7. Structure of Pyridine.—(1) Molecular formula of pyridine deduced from its analytical data and molecular weight determination is C_5H_5N.

(2) *Pyridine resembles benzene in many of its properties and thus exhibits aromatic character.* For example,

(*i*) It is extremely stable towards oxidising agents like potassium permanganate, chromic acid and nitric acid.

(*ii*) Apparently an unsaturated compound, it gives substitution products with chlorine and bromine.

(*iii*) It can be nitrated and sulphonated.

(*iv*) Its amino derivatives can be diazotised and coupled in the usual way.

(*v*) Its hydroxy derivatives exhibit true phenolic properties.

(*vi*) Alkylpyridines yield pyridinecarboxylic acids on oxidation.

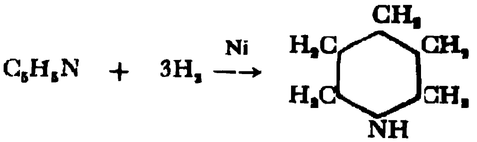
(3) It combines with alkyl halides on heating to give quaternary salts, *e.g.*, *N*-methylpyridinium iodide is formed with methyl iodide.

$$C_5H_5N \xrightarrow[\text{Heat}]{CH_3I} C_5H_5\overset{+}{N}CH_3]\overset{-}{I}$$

N-methylpyridinium iodide

This suggests the presence of a tertiary nitrogen atom in the molecule.

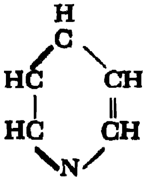
(4) On catalytic reduction pyridine adds three molecules of hydrogen to give piperidine, a ring compound.



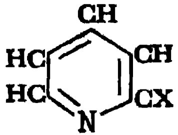
Piperidine

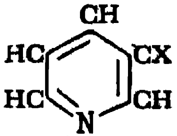
This suggests the presence of ring containing five carbon atoms and a tertiary nitrogen atom. Addition of six hydrogen atoms suggests the presence of three double bonds.

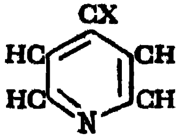
(5) Keeping these facts in view Korner (1864) suggested the following ring structure for pyridine :



(6) Taking this as the formula of pyridine, there are three possible monosubstitution products given below :


2-Deriv.

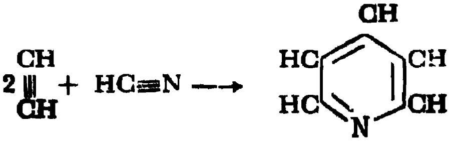

3-Deriv.


4-Deriv.

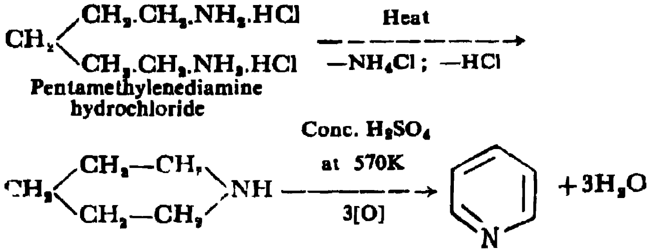
Pyridine actually gives three monosubstitution products and supports the proposed structure for pyridine.

(7) This formula is further confirmed by the following synthesis of pyridine.

(*i*) *By passing a mixture of acetylene and hydrogen cyanide through a red hot tube.*



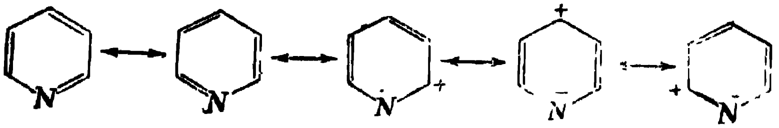
(*ii*) *By heating pentamethylenediamine hydrochloride when piperidine is obtained and oxidising the latter with concentrated sulphuric acid at 570K.*


Pentamethylenediamine hydrochloride

Piperidine

Pyridine

(8) Present view about the structure is that pyridine is a resonance hybrid of the following two Kekulé structures and three charged structures. Its resonance energy is about 125·5 kJ mol^{-1}.


I II III IV V

In all of these the lone pair of nitrogen atom is free to unite with a proton. This explains the formation of salts and quaternary compounds.

In the orbital picture of pyridine, the nitrogen atom like each of the five carbon atoms is bonded to two other members of the ring by the use of two sp^2 orbitals and provides one electron for the π cloud. In the case of carbon the third sp^2 orbital is used for

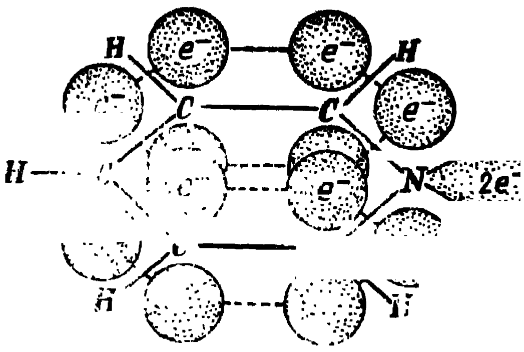
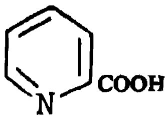


Fig. 47·3—Orbital structure of pyridine with π electron clouds above and below the plane of pyridine ring and unshared pair of electron with nitrogen atom.

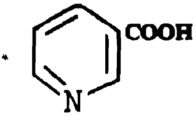
bonding hydrogen whereas in the case of nitrogen it simply contains a pair of electrons available for sharing with acids. This makes pyridine a much stronger base than pyrrole.

8. Homologues and Derivatives of Pyridine.—Three methylpyridines called **picolines** are known. Six dimethylpyridines (called **lutidines**) and six trimethylpyridines (called **collidines**) are also known. Monohydroxypyridines are called **pyridols**. 3-Hydroxypyridine exhibits true phenolic properties.

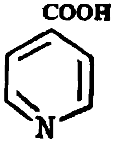
Three monocarboxylic acids are :



Picolinic acid

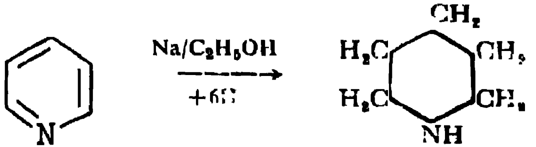


Nicotinic acid



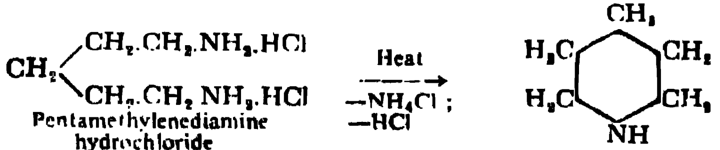
Iso-Nicotinic acid

9. Piperidine, $C_5H_{10}NH$.—It occurs in the alkaloid piperine and may be prepared by reducing pyridine with sodium and ethanol, electrolytically or catalytically using nickel catalyst.



Pyridine Piperidine

It may also be prepared by heating pentamethylenediamine hydrochloride

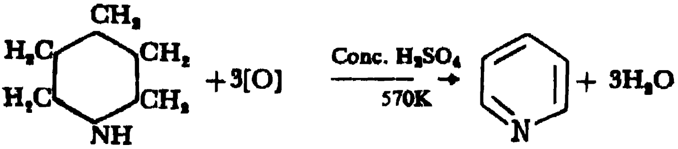


Pentamethylenediamine hydrochloride

Piperidine

Properties and Uses. Piperidine is a colourless liquid (b.p. 379K) with a pepper-like smell. It is soluble in water, alcohol and

It is a stronger base as compared with pyridine and gives the reactions of a secondary aliphatic amine. When heated with concentrated sulphuric acid at 570K, it is oxidised to pyridine.



It is used as an accelerator in the vulcanization of rubber

QUESTIONS

Essay Type :

1. Explain the meaning of heterocyclic compounds. Give three examples drawn from the aliphatic series. Name three five-member heterocyclic compounds and compare their mode of preparation and properties.

2. How would you prepare furan ? What are its properties ?

3. Why would you expect furan to give electrophilic substitution reactions ? Write down the principal canonical structures for the intermediate (or complex) involved at 2 and 3 substitutions of furan by an electrophilic reagent. *(Delhi B.Sc. Hons 1982)*

4. Write the resonance structures of pyrrole, pyridine and thiophene. How is thiophene separated from benzene and how do you test for thiophene in benzene ? Write any other method used for its manufacture and mention its properties. *(Bangalore B.Sc. 1974)*

5. (*a*) Enumerate the important methods for the synthesis of pyrrole and its main chemical properties. *(Burdwan B.Sc. 1971)*

(*b*) Give principal products of reaction of pyrrole with the following reagents :

(*i*) Nitric acid in acetic anhydride at —10°C.

(*ii*) Chromium trioxide in sulphuric acid.

(*iii*) Potassium iodide-iodine solution.

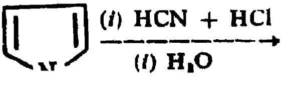
(*iv*) Benzenediazonium chloride. *(G.N.D. B.Sc. 1982)*

6. Describe the synthesis of the following compounds :

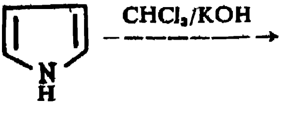
(*a*) Furan, (*b*) Thiophene, (*c*) Pyrrole, (*d*) Quinoline. *(Utkal B.Sc. 1976)*

7. Name the following reactions and write down the products formed in each case :

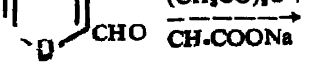
(*i*)



(*ii*)



(*iii*)



(Delhi B.Sc. Hons. 1982)

8. Describe the structure of pyridine. How can it be converted into (*a*) piperidine, (*b*) *n*-pentane, (*c*) 3-nitropyridine ? (*Delhi B.Sc. Hons. Sub. 1977 Supp.*)

9. Why is pyridine basic ? Discuss the behaviour of pyridine towards electrophilic and nucleophilic reagents. (*Andhra B.Sc. 1978*)

10. Discuss fully the structure of pyridine What happens when it is treated with (*a*) Bromine, (*b*) Hot conc sulphuric acid, and (*c*) Sodium in ethanol ? (*Delhi B.Sc. 1976 Supp*)

11. What are heterocyclic compounds ? How is pyridine isolated from coal-tar ? How does pyridine react with (*i*) hot conc H_2SO_4, (*ii*) Na/C_2H_5OH, (*iii*) Br_2 ? (*Delhi B.Sc. 1980*)

12. What is pyridine ? How is it prepared from an open-chain amine ? What is the reaction of pyridine with the following reagents :

(*i*) Sodamide, (*ii*) Butyllithium, (*iii*) Bromine/carbon catalyst, (*iv*) Nitric acid, (*v*) Peracids ?

How is the size of a nitrogen heterocyclic ring determined ? (*Delhi B.Sc. 1979 Supp.*)

13. (*a*) What reactions would you perform to show the presence of tertiary nitrogen in pyridine.

(*b*) How would you explain that pyridine acts like a deactivated benzene ring ? (*Delhi B.Sc. Hons. 1982*)

Short Answer Type :

1. Write the formulae for the following compounds :

(*i*) 3-Chlorofuran. (*ii*) 2-Ethoxythiophene. (*iii*) 2-Methylthiophene. (*iv*) 3-Chlorofuran. (*v*) 3-Ethylfurfural. (*vi*) 3-Hydroxypyridine, (*vii*) 3-Methylpyrrole. (*viii*) 3-*tert*. Butylpyridine

2. How will you prepare the following :

(*a*) Furan from mucic acid. (*b*) Furil from furfural.
(*c*) 1-Pyrrolecarboxylic acid. (*d*) Pyridine from acetylene.
(*e*) Pyrrole from succinimide. (*f*) Furan from furfural.
(*g*) Pyridine from 1, 5-pentanediamine

3. Complete the following sequence of operations and also give the end products:

(*i*) Phenol+Acetyl chloride $\longrightarrow$ (A) $\xrightarrow{\text{Anhy. AlCl}_3}$?

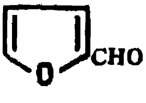
(*ii*) Pyridine $\xrightarrow{\text{Na+EtOH}}$ (A) $\xrightarrow{CH_3I}$ (B) $\xrightarrow{\text{AgOH}}$ (C) $\xrightarrow{\text{Heat}}$

(D) $\xrightarrow[(ii)\ \text{AgOH}\ (iii)\ \text{Heat}]{(i)\ CH_3I}$? (*Bombay B.Sc. 1971*)

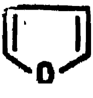
4. Pyrrole is more reactive than furan. Explain, why.

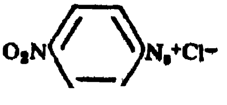
5. Pyrrole is much more acidic than dimethylamine. Give reasons.

6. Complete the following equations :

(*i*) 

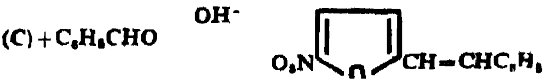
+ $(CH_3CO)_2O \xrightarrow{CH_3COONa}$ (A)

(*ii*) 

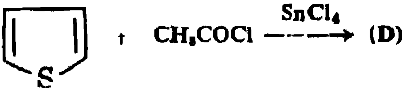
+ 

$\xrightarrow{OH^-}$ (B)

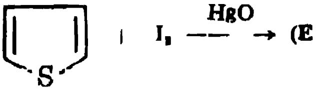
(*iii*)



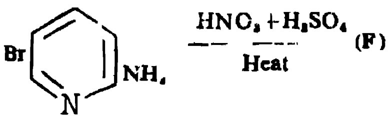
(*iv*)



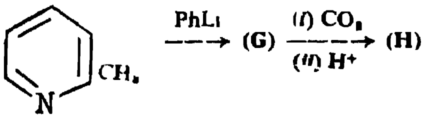
(*v*)



(*vi*)



(*vii*)



7. Give structural formula and name of a compound containing a sulphur atom in the ring and another with a nitrogen atom in the ring.
(*Punjab B.Sc. 1976*)

8. Why is pyridine more basic than pyrrole ?
(*Guru Nanak Dev B.Sc. 1977 ; Delhi B.Sc. Hons. 1976*)

9. Electrophilic substitution in furan occurs preferentially at α-position. Explain.
(*Guru Nanak Dev B.Sc. 1977*)

10. How can pyridine ring be cleaved ? (*Bangalore B.Sc. 1974*)

11 Pyridine does not undergo Friedel-Crafts reaction. Explain, why.
(*Andhra B.Sc. 1974*)

12. Give the structures of the product or products in the following reactions

(*a*) Pyrrole $\xrightarrow{CHCl_3,\ KOH}$ (*b*) Thiophene $\xrightarrow{CH_2O,\ HCl}$

(*c*) Furan+Maleic anhydride ⟶ (*Andhra B.Sc. 1974*)

13. Write the resonance structures of pyrrole. (*Bangalore B.Sc. 1974*)

14. Give two similar reactions between pyrrole and phenol
(*Bangalore B.Sc. 1974*)

15. How would you account for the fact : Nitration of pyridine gives mainly 3-nitropyridine, but $NaNH_2$ gives 2-aminopyridine.
(*Delhi B.Sc. Hons. 1975*)

16. Explain basic character of pyridine. (*Delhi B.Sc. 1976*)

17. How will you show that :

(*i*) Furan behaves like on aromatic compound.

(*ii*) Substitution in the Pyridine ring takes place at 3-position during electrophilic attack and at 2-position when the attack is nucleophilic ?

(*iii*) Pyrrole possesses properties in common with both phenols and aromatic amines ? (*Delhi B.Sc. Hons. 1976*)

18. How will you convert furan to 2-acetylfuran ? (*Andhra B.Sc. 1978*)

19. What happens when

(*a*) Pyridine is treated with sodamide,

(*b*) Pyridine is treated with phenyllithium, (*c*) Pyrrole is treated with *p*-nitrobenzene-diazonium chloride ? (*Madras B.Sc. 1978*)

20. Discuss the basicity of pyridine. (*Kurukshetra B.Sc. 1978 Supp.*)

21. How will you arrive at the structure of pyridine ? (*Kurukshetra B.Sc. 1978*)

22. Discuss electrophilic and nucleophilic substitution reactions of pyridine. (*Kurukshetra B.Sc. 1978*)

23. What happens when pyridine is treated with bromine at 770K ? (*Kurukshetra B.Sc. 1977 Supply*

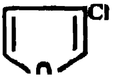
24. (*a*) Compare the reactivity of pyrrole with pyridine.

(*b*) How do you account for the aromatic character in thiophene ?

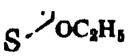
(*c*) How is pyridine *N*-oxide obtained ? Give its various resonating structures. (*Delhi B.Sc. Hons. 1979*)

ANSWERS

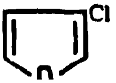
1. (*i*)



(*ii*)



(*iv*)



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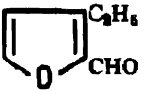
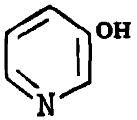
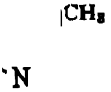
(*v*)



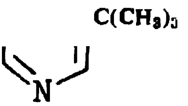
(*vi*)



(*vii*)



(*viii*)



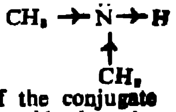
4. (*a*) Electrophilic substitution in both of them occurs preferentially in 2- (or 5-) position. Electron density is higher in this position (see pages 3·45-46 and 3·57). However, since oxygen is more electronegative than nitrogen, electron-withdrawing effect from these positions is expected to be greater in furan than in pyrrole. As a result of it 2- (or 5-) position in pyrrole has higher electron density than in furan.

Reference to resonance hybrid structures will show that oxygen atom in furan and nitrogen atom in pyrrole carry positive charge. Here again oxygen being more electronegative than nitrogen, resonating structures of furan in which oxygen carries positive charge will be expected to make smaller contribution.

Hence as compared with pyrrole, electron-withdrawal is greater and electron-donation is smaller in furan. Combined effect of these two factors results in higher electron density in position 2- (or 5-) in pyrrole which is, therefore, more readily substituted or in other words is more active.

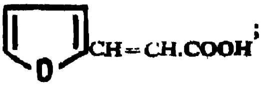
We can explain the same thing on the basis of stability of the concerned carbocation. In these oxygen and nitrogen atoms carry positive charge. But since nitrogen tom, being less electronegative, can accommodate the positive charge more readily, pyrrole carbocation is more stable than the furan carbocation. Hence the former is produced more readily than the latter. In other words, pyrrole is more reactive than furan.

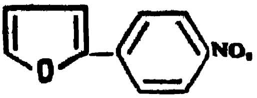
5. In dimethylamine proton release is hindered because of the +I effect of the methyl groups. On the other hand in the resonance hybrid structure of pyrrole (Page 3·55), the nitrogen atom carries a positive charge and this facilitates the release of a proton. Hence pyrrole is more acidic than dimethylamine.

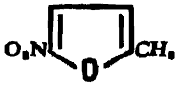


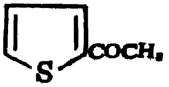
$$CH_3 \rightarrow \ddot{N} \rightarrow H \atop {\uparrow \atop CH_3}$$

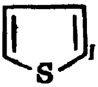
This could also be explained in terms of the stability of the conjugate base. Conjugate base of pyrrole being a resonance hybrid is more stable than the conjugate base of dimethylamine. Hence pyrrole is much more acidic than dimethylamine.

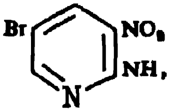
6. (*i*) (A) is 

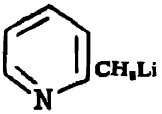
; (*ii*) (B) is 

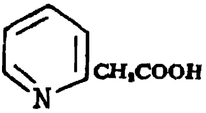
(*iii*) (C) is 

; (*iv*) (D) is 

(*v*) (E) is 

; (*vi*) (F) is 

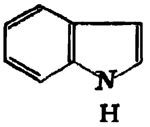
(*vii*) (G) is 

; (*viii*) (H) is 

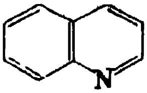
4

Heterocyclic Compounds—(ii)

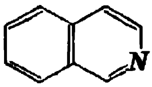
1. Condensed Ring Systems.—The heterocyclic compounds studied in the last chapter were simple ones and each contained one heterocyclic ring. There are some more important heterocyclic compounds in which a benzene ring is condensed with a five or six-member heterocyclic ring, *e.g.*, indole, quinoline and isoquinoline.



Indole

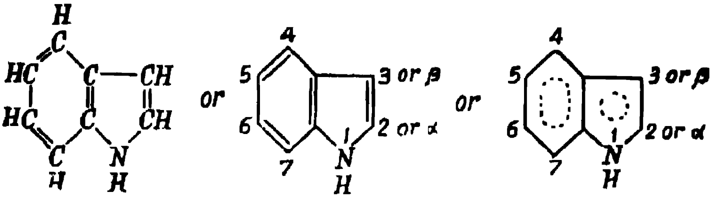


Quinoline



Isoquinoline

2. Indole, 1*H*-1-Azaindene Benzopyrrole, C_8H_7N.—The molecule of indole is made up of a benzene ring fused with a pyrrole ring. To name its derivatives various atoms of indole are numbered as follows :

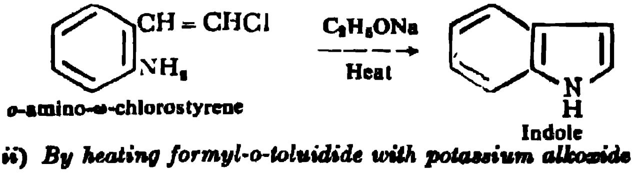


Resonance hybrid structure

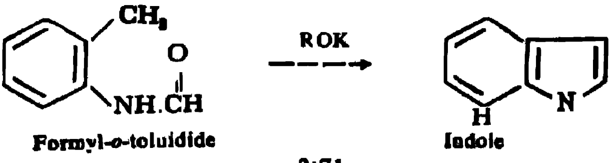
It occurs in coal-tar, jasmine flowers and orange blossoms. It is the parent substance of indigo.

Synthesis. Indole may by synthesised by any of the following methods :

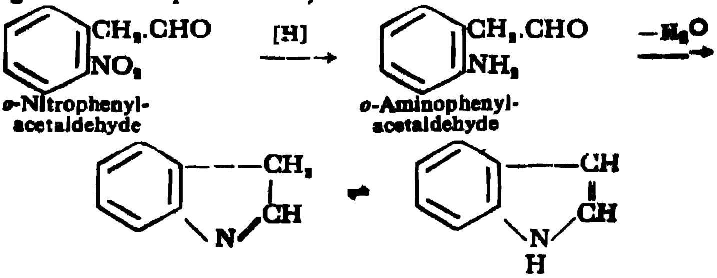
(*i*) *Lipp's synthesis* (1884). *By heating o-amino-ω-chlorostyrene with sodium ethoxide.*



(*ii*) ***By heating formyl-o-toluidide with potassium alkoxide***



(*iii*) *By reduction of o-nitrophenylacetaldehyde with iron powder and sodium bisulphite solution*. The amino compound produced changes to indole spontaneously.



o-Nitrophenyl-acetaldehyde

o-Aminophenyl-acetaldehyde

Indolenine formula

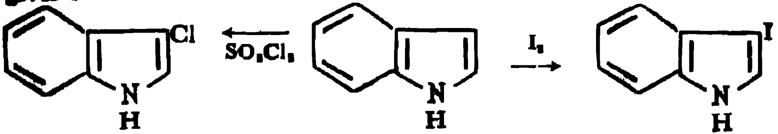
Ordinary Indole formula

Properties. Indole is a crystalline solid (m.p. 325K) giving plate-like crystals Impure indole has a strong unpleasant faecal odour while pure indole in dilute solutions has pleasant smell and is used in perfumery for preparing jasmine and orange blossom blends.

Chemically indole resembles pyrrole in many of its properties It is oxidised by ozone to indigotin. Indole solution imparts a cherry-red colour to pine shavings moistened with alcohol and hydrochloric acid.

Electrophilic substitution in indole normally occurs in the 3-position. However, if this position is blocked, substitution takes place in 2-position and if both 2- and 3-positions are occupied, substitution occurs in the benzene ring at 6-position. For example,

(*i*) It is brominated or iodinated in 3-position. With SO_2Cl_2, it gives 3-chloroindole.

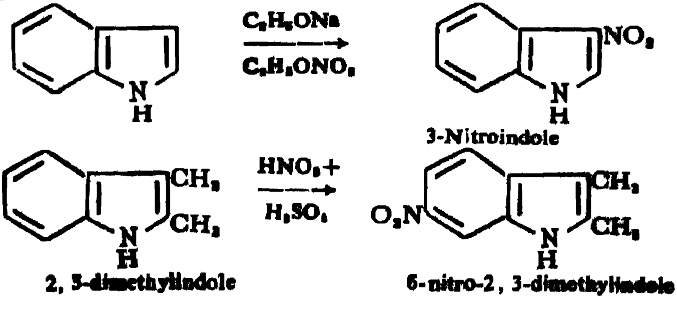


3-Chloroindole

Indole

3-Iodoindole

(*ii*) On treating indole mixed with sodium ethoxide with ethyl nitrate, 3-nitroindole is obtained. On the other hand, nitration of 2, 3-dimethylindole with acids mixture gives the corresponding 6-nitro derivative.

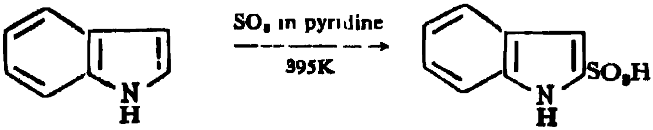


3-Nitroindole

2, 3-dimethylindole

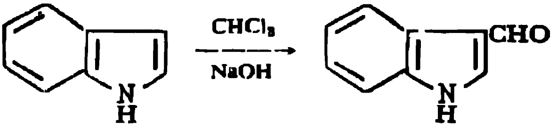
6-nitro-2, 3-dimethylindole

(*iii*) On treating indole with SO_3 in pyridine at about 390K 2-indole sulphonic acid is produced. It is rather an unusual case of orientation.



2 Indole-sulphonic acid

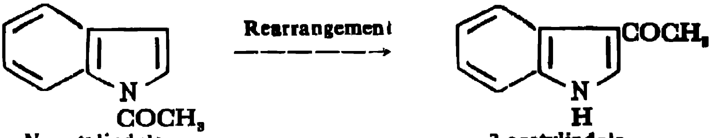
(*iv*) Reimer-Tiemann reaction gives indole-3-aldehyde



Indole 3-Indolecarbaldehyde

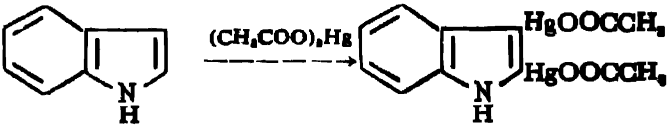
This compound may also be prepared by Gattermann aldehyde synthesis.

(*v*) *N*-acetylindole undergoes rearrangement to give 3-acetylindole.



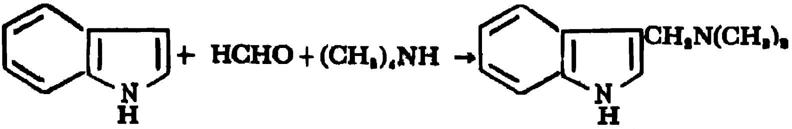
N-acetylindole 3-acetylindole

(*vi*) *Mercuration.* On mercuration with mercuric acetate, Indole gives 2, 3-diacetoxymercuri-indole.



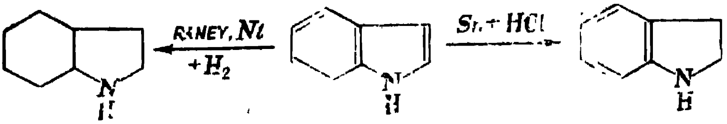
(*vii*) Indole forms a Grignard reagent readily which can be used for the preparation of a number of substituted indoles.

(*viii*) *Mannich reaction.* Indole reacts with formaldehyde and dimethylamine to give gramine (3-dimethylaminomethylindole).



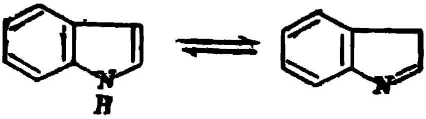
Indole Gramine

(*ix*) ***Reduction.*** Indole on electrolytic reduction gives 2, 3-dihydroindole (*indoline*). Reduction with metal and acid (Sn+HCl or zinc dust + H_3PO_4) gives the same product. Catalytic reduction with Raney nickel gives octahydroindole



Octahydroindole 2, 3 dihydroindole

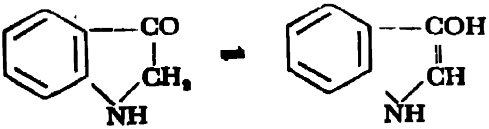
Indole behaves as tautomer of *Indolenine.*



Indole **Indolenine**

Indolenine itself has never been isolated but its derivatives are known.

3. **Indoxyl.**—Indoxyl and 3-Hydroxyindole are two tautomeric compounds in which indoxyl is the keto-form and 3-hydroxyindole is the enolic form.

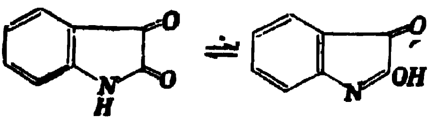


Indoxyl **3-Hydroxyindole**
(*keto-form*) (*Enolic-form*)

Indoxyl occurs as *indican* (a glucoside) in indigo plant. It may be prepared by hydrolysis of indican or is synthesised (*Refer to page* 3·84)

Indoxyl is a bright yellow solid (m.p. 358K). An alkaline solution of indoxyl is readily oxidised by air to indigotin.

4. **Isatin.**—It occurs in two tautomeric forms I and II (both derivatives of 2 : 3-dihydroindole).

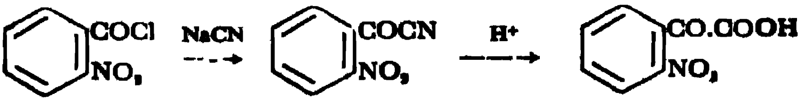


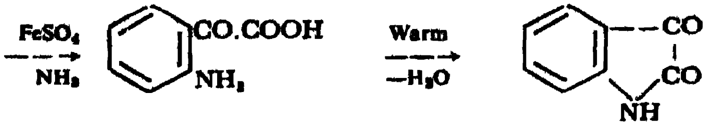
I II

This is an example of ***amido-imidol*** tautomeric system.

$$—NH—CO— \rightleftharpoons —N{=}C(OH)—$$

It was first prepared by oxidation of indigotin with nitric acid but can be synthesised as follows :

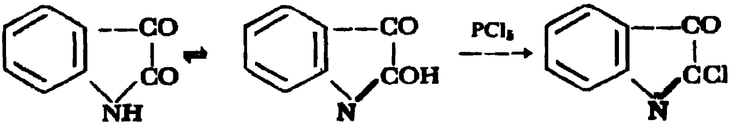




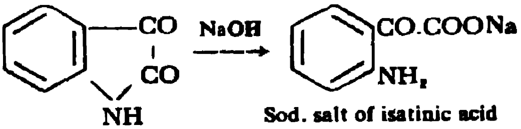
Isatin

The synthesis shows the structure of isatin.

It is a red crystalline solid (m.p 473K) slightly soluble in water but readily soluble in alcohol It reacts with PCl_5 to form ***isatin chloride*** and with warm solution of sodium hydroxide to give **sodium salt of *isatinic acid.***



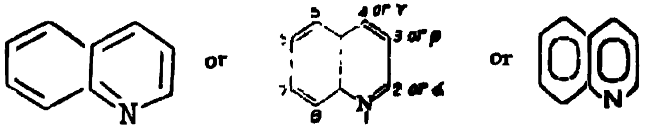
Isatin chloride



Sod. salt of isatinic acid

Isatin

5. **Quinoline**, **1-Azanaphthalene**, **α, β-Benzopyridine**, **C_9H_7N.** —Quinoline is another example of a fused ring system in which a benzene ring is fused with a pyridine ring in α-, β-positions. To name its derivatives various atoms are numbered as follows :



Quinoline

Resonance hybrid structure

Quinoline is present in coal-tar and bone oil. It was first prepared by Gerhardt (1842) by distilling the alkaloid quinine with alkali and hence named quinoline,

Preparation. Quinoline is obtained commercially from coal-tar or prepared synthetically as follows :

Skraup synthesis (1880). *By heating a mixture of aniline, nitrobenzene, glycerol, concentrated sulphuric acid and ferrous sulphate.* In this mixture nitrobenzene acts as an oxidising agent while presence of ferrous sulphate makes the reaction less violent. When nitrobenzene brings about oxidation, it itself is reduced to aniline. Other mild oxidising agents like H_3AsO_4 can replace nitrobenzene.

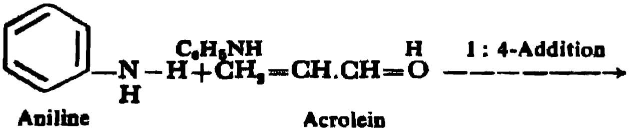
The mechanism of the reaction is not certain. It is, however, believed to be as under :

(*i*) Glycerol loses water to yield acrolein (having a conjugated system of double bonds).

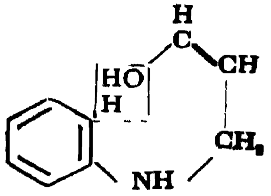
(ii) Aniline adds on to acrolein in the 1 : 4-position.

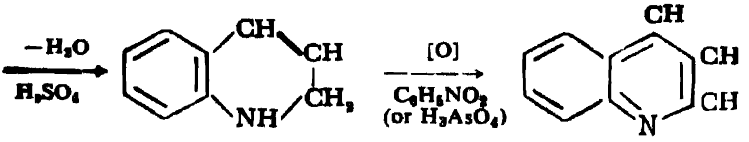
(*iii*) The side-chain is condensed in the *o*-position to yield dihydroquinoline which on oxidation gives quinoline. The yield is about 84-91%.

$$\underset{\text{Glycerol}}{CH_2OH.CHOH.CH_2OH} \xrightarrow[H_2SO_4]{-2H_2O} \underset{\text{Acrolein}}{CH_2{=}CH.CH{=}O}$$



$C_6H_5NH.CH_2-CH=CH.OH$ or



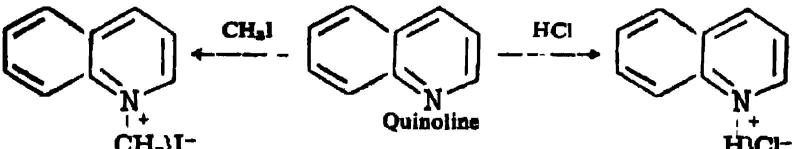


1 : 2-Dihydroquinoline Quinoline

Properties : Physical. Quinoline is a colourless oily liquid (b.p 511K) sparingly soluble in water but readily dissolves in alcohol and ether. It has characteristic disagreeable smell but not so unpleasant as that of pyridine. It is volatile in steam.

Chemical . Being made up of a benzene ring and a pyridine ring quinoline gives some reactions of the benzene ring and some of the pyridine ring.

(1) **Basic nature.** Quinoline is a tertiary base and resembles pyridine in many of its reactions. It forms quinolinium salts with inorganic acids and quaternary salts with alkyl halides.



Quinoline methyl iodide or *N*-methyl quinolinium iodide

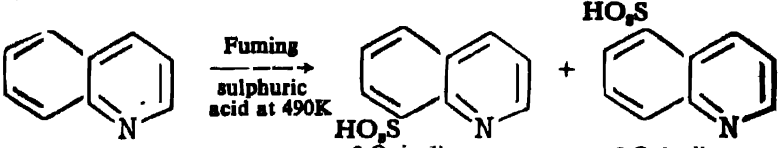
Quinoline

Quinoline hydrochloride

(2) **Substitution Reactions.** Quinoline is a resonance hybrid with resonance energy of 264·9 kJ mol⁻¹. The nitrogen atom deactivates the pyridine ring. Quinoline resembles 1-nitronaphthalene in many respects. It is attacked by electrophilic reagents preferentially at position 8 and by nucleophilic reagents at positions

2 and 4. In other words, the electrophilic reagents usually attack the benzene ring while the nucleophilic reagents attack the pyridine ring preferentially. For example :

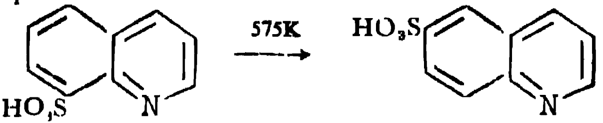
(*i*) **Sulphonation.** Fuming sulphuric acid at 490K yields 8-quinoline sulphonic acid with a small amount of 5-quinoline-sulphonic acid.



8-Quinoline-sulphonic acid (*Main product*)

5-Quinoline-sulphonic acid (*Small quantity*)

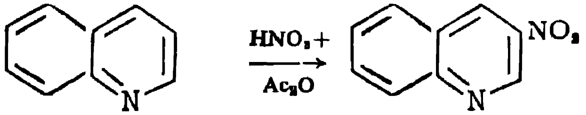
When 8-sulphonic acid is heated to 570K, it rearranges to give 6-sulphonic acid.



8-sulphonic acid

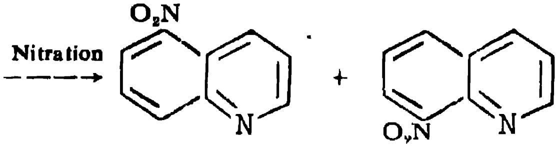
6-sulphonic acid

(*ii*) **Nitration.** Quinoline yields on nitration with acids mixture a mixture of 5- and 8-nitroquinoline. But nitration with nitric acid and acetic anhydride gives 3-nitroquinoline.



Quinoline

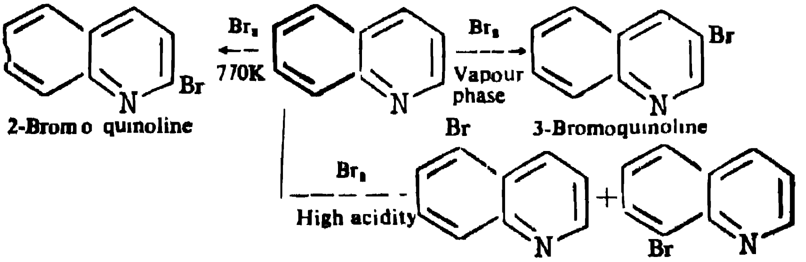
3-Nitroquinoline



5-Nitro quinoline

8-Nitro quinoline

(*iii*) **Bromination.** Vapour phase bromination of quinoline gives 3-bromoquinoline. At 770K, however, the product is 2-bromoquinoline. Bromination under conditions of high acidity produces 5- and 8-bromoquinolines.



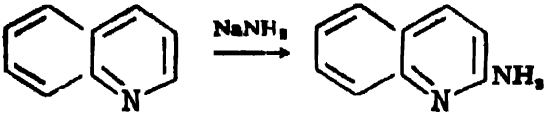
2-Bromo quinoline

3-Bromoquinoline

5-Bromo quinoline

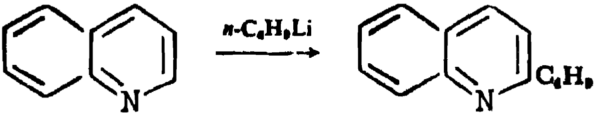
8-Bromo quinoline

(*iv*) **With sodamide.** Quinoline on heating with sodamide in toluene solution gives 2-*aminoquinoline* (*Tschitschibaben reaction*)



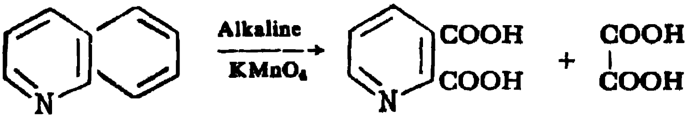
2-Aminoquinoline

(*v*) **With *n*-butyl-lithium.** Quinoline reacts with *n*-butyl-lithium to give 2-butyl derivative.



2-butylquinoline

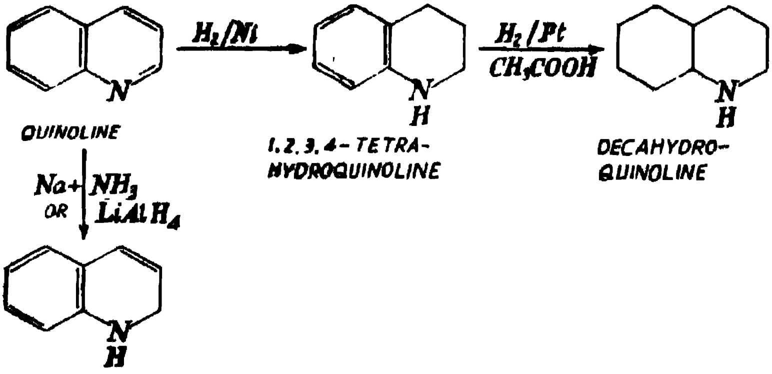
(3) **Oxidation.** Vigorous oxidation as with alkaline permanganate usually oxidises away the benzene ring with the formation of quinolinic acid and oxalic acid.



Quinoline Quinolinic acid

With perbenzoic acid quinoline is oxidised to 1-oxide.

(4) **Reduction.** Reducing agents like sodium in liquid ammonia or lithium aluminium hydride reduce it to 1, 2-dihydroquinoline. With tin and hydrochloric acid or controlled hydrogenation at 430K gives tetrahydroquinoline, whereas catalytic reduction using platinum as catalyst in acetic acid solution yields decahydroquinoline.



QUINOLINE

1,2,3,4-TETRA-HYDROQUINOLINE

DECAHYDRO-QUINOLINE

1,2-DIHYDRO-QUINOLINE

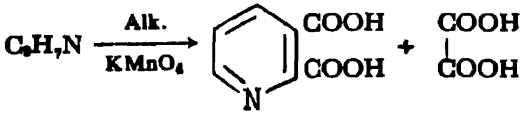
Uses of Quinoline. Quinoline finds use (*i*) as a high-boiling solvent ; (*ii*) as an antiseptic ; (*iii*) in analytical work for precipitation of certain metals.

6. **Constitution of Quinoline**.—(*i*) Molecular formula of quinoline as deduced from its analytical data and molecular weight determination is C_9H_7N.

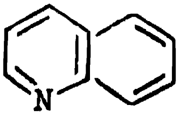
(*ii*) Quinoline undergoes nitration and sulphonation just like benzene. This indicates the presence of one or more aromatic rings in the molecule.

(*iii*) It forms quaternary salts with alkyl halides. This suggests the presence of a tertiary nitrogen atom in it.

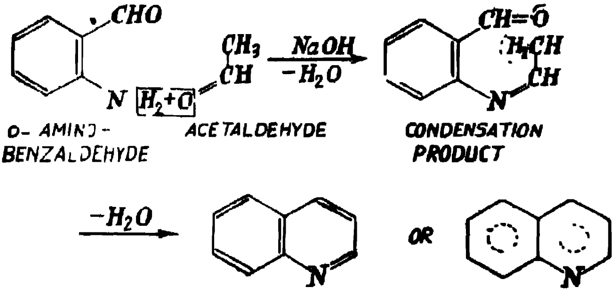
(*iv*) On vigorous oxidation with alkaline permanganate it gives quinolinic acid and oxalic acid.



On the analogy of naphthalene which on oxidation gives phthalic acid, we can conclude that in quinoline one pyridine ring is fused with a benzene ring which is broken during oxidation. Thus the structural formula of quinoline may be written as

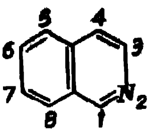


(*v*) This structure is further confirmed by **Friedlander's synthesis** (1882) of quinoline by condensing *o*-amino-benzaldehyde with acetaldehyde in aqueous sodium hydroxide.

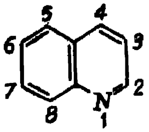


Quinoline

7. **Isoquinoline, C_9H_7N.**—Like quinoline the molecule of isoquinoline is made up of a benzene ring fused with a pyridine rin ut in a different position as given below :



Isoquinoline

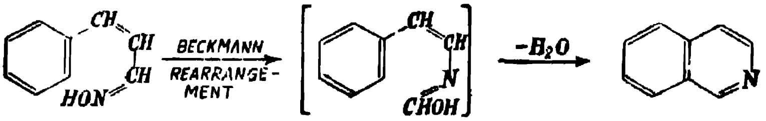


Quinoline

These two heterocycles are numbered like the naphthalene molecule in such a way that the hetero atom has the smallest possible number.

Preparation. Isoquinoline is always present in quinoline and may be separated from there. The mixture is converted into sulphates which are separated by fractional crystallization from alcohol in which isoquinoline sulphate is only sparingly soluble.

It may be synthesised in a number of ways. One simple way is by heating the oxime of cinnamaldehyde with phosphorus pentoxide.



The oxime first undergoes Beckmann rearrangement and the product undergoes ring closure by losing a molecule of water.

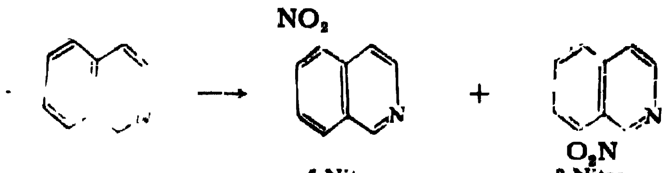
Properties. Isoquinoline is a colourless solid (m.p. 296K, b.p. 513K) having an odour resembling benzaldehyde.

Chemically, it resembles quinoline in many of its properties. For example :

(1) **Basic nature.** It is a stronger base as compared with quinoline and gives quaternary salts with alkyl halides.

(2) **Electrophilic Substitution.** Isoquinoline resembles 2-nitronaphthalene in a number of its properties. Electrophilic substitution occurs predominantly at 5-position and to a small extent at 8-position. For example :

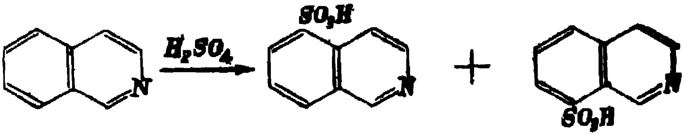
(*i*) **Nitration.** On nitration the main product obtained is 5-nitroisoquinoline together with a small quantity of 8-derivative



5-Nitro-isoquinoline

8-Nitro-isoquinoline

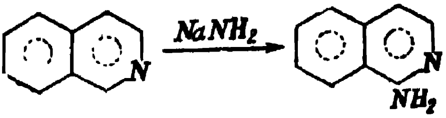
(*ii*) **Sulphonation.** Sulphonation also takes place mainly at the 5-position and to a small extent at 8-position.



5-DERIV. 8-DERIV.

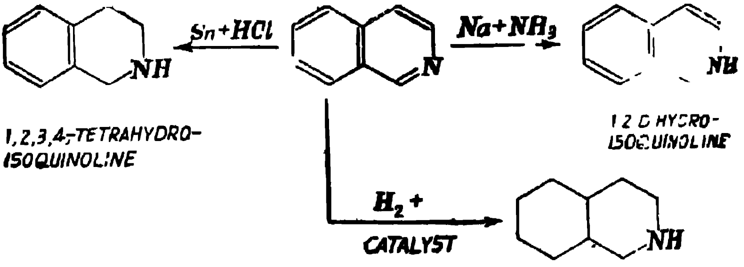
(iii) **Bromination and Mercuration.** On bromination isoquinoline gives predominantly 4-bromo-isoquinoline. Similarly, 4 derivative is obtained on mercuration with mercuric acetate.

(3) **Nucleophilic Substitution.** Nucleophilic substitution in isoquinoline occurs at position 1. For example, when treated with sodamide it gives 1-amino-isoquinoline.



1-Aminoisoquinoline

(4) **Reduction.** Isoquinoline on reduction with sodium and liquid ammonia gives 1, 2 dihydroisoquinoline. With tin and hydrochloric acid the reduction product is 1, 2, 3, 4-tetrahydroisoquinoline whereas catalytic hydrogenation gives octahydroisoquinoline.

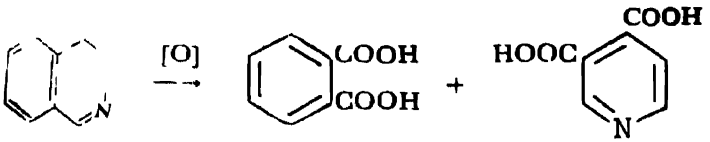


1,2,3,4-TETRAHYDRO-ISOQUINOLINE

1 2 DIHYDRO-ISOQUINOLINE

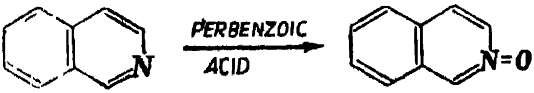
OCTAHYDRO-ISOQUINOLINE

(5) **Oxidation** Pyridine ring in isoquinoline is not so stable as in quinoline On oxidation with permanganate it yields a mixture of phthalic and cinchomeronic acids



Isoquinoline Phthalic acid Cinchomeronic acid

With perbenzoic acid isoquinoline is oxidised to the *N*-oxide.

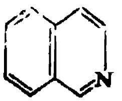


Constitution. (*i*) Molecular formula of isoquinoline as deduced from its analytical data and molecular weight determination is C_9H_7N.

(*ii*) Isoquinoline undergoes nitration like benzene. This indicates the presence of one or more aromatic rings in the molecule.

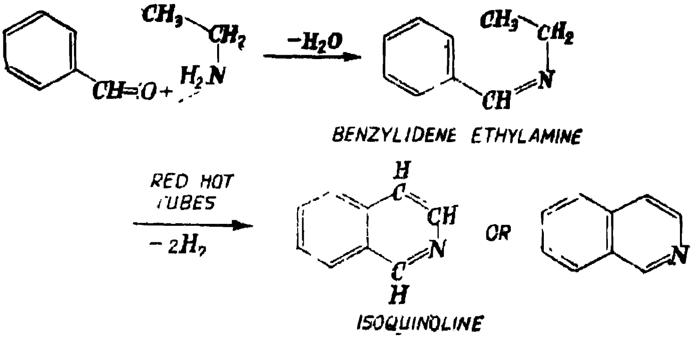
(*iii*) With alkyl halides it yields quaternary salts. This suggests the presence of a tertiary nitrogen atom in it.

(*iv*) On oxidation with permanganate it yields a mixture of phthalic acid and cinchomeronic acid (*see* above). This shows that isoquinoline molecule consists of one benzene ring fused with a pyridine ring in βγ-positions. Phthalic acid is produced when pyridine ring gets ruptured and cinchomeronic acid is produced when benzene ring is ruptured. Positions of the two carboxylic groups in cinchomeronic acid indicate the position in the pyridine ring (βγ) where it is fused with the benzene ring. Hence, molecule of isoquinoline is given by the structural formula given below :



Isoquinoline

(*v*) This structure is further confirmed by syntheses of isoquinoline by condensing benzaldehyde with ethylamine and passing vapours of the product (benzylidene ethylamine) through red hot tubes



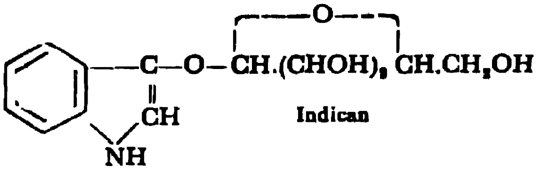
8. **Indigo, Indigotin,** $C_{16}H_{10}O_2N_2$.—Of all dyes, natural or synthetic, indigo is the oldest known dye. Egyptian mummy clothes estimated to be over four thousand years old were dyed with it. It is a mixture of several dyes, the chief component being *indigotin* with small quantities of indigo red and indigo brown. India appears to be the birth-place of indigo.

Indigo occurs as a glucoside, *indican* in many plants, *e.g.*, indigo plant (*Indigofera* species) grown in tropical countries like India. Small amounts of indican are present in *woad*, an impure form of indigotin, and is obtained from the plant *isatis tinctoria* grown in the European countrie. It is believed that the art of cultivation and methods of application had spread to the ancient Indo-Germanic tribes in Europe from India. India cultivated 2,50,000

acres of land for indigo and exported Rs. 70,00,000 worth indigo in 1897. Synthetic indigotin has ruined the Indian indigo industry.

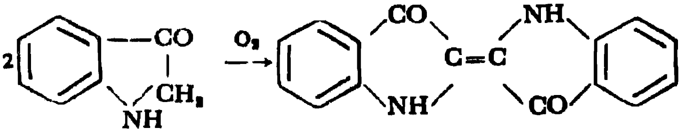
Preparation of Indigotin

(1) **From Indigo Plants.** Indigo plants contain **indican, a** glucoside of indoxyl :


Indican

The glucoside is extracted from the plant with water. Its hydrolysis, promoted by the enzymes of the plant, gives **indoxyl** which is oxidised by the oxygen of the air to indigo.

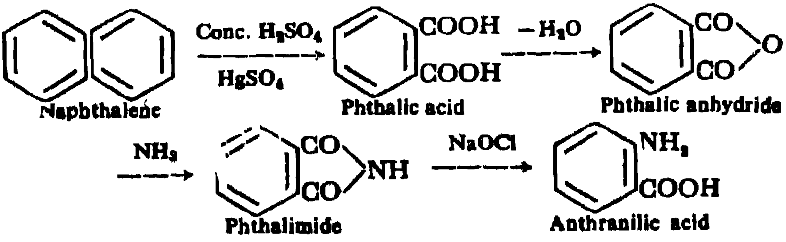
$$\underset{\text{Indican}}{C_{14}H_{17}NO_6} + H_2O \longrightarrow \underset{\text{Indoxyl}}{C_8H_7NO} + \underset{\text{Glucose}}{C_6H_{12}O_6}$$


Indoxyl Indigotin

Indigo plants are cut shortly before flowering and placed in wooden tanks. Warm water at 298-300K is added to the tank. On standing fermentation sets in and the enzyme *indimulsase* (present in the leaves) brings about hydrolysis of indican to indoxyl. The fermented liquor containing indoxyl is made alkaline by adding lime and churned vigorously by bubbling air. Passage of air oxidises indoxyl to indigotin containing traces of indigo red and indigo brown. This separates as blue flakes. The flakes are separated, boiled with water and filter-pressed. The cake thus obtained is indigo.

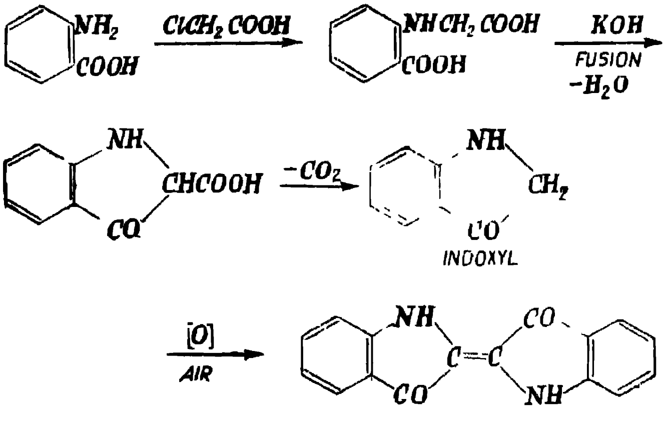
(2) **Commercial Synthesis.** Very little indigo is at present manufactured from the plants as the synthetic processes have proved to be cheaper. Different synthetic methods employed for the manufacture of indigo are :

(*a*) **From Anthranilic acid.** This method was developed in 1897 in Germany. Anthranilic acid is produced from naphthalene through phthalic anhydride and phthalimide.

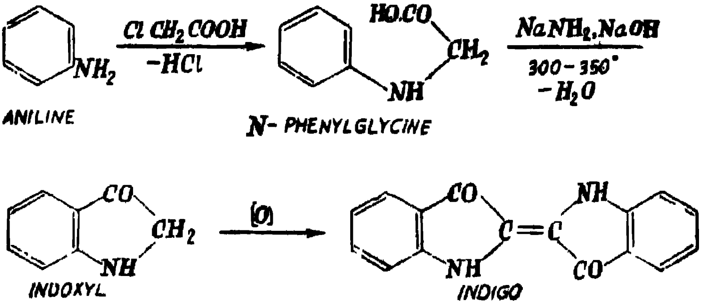


Naphthalene Phthalic acid Phthalic anhydride Phthalimide Anthranilic acid

Anthranilic acid is converted to phenylglycine-*o*-carboxylic acid with chloroacetic acid. This on fusion with potassium hydroxide yields indoxylic acid which loses carbon dioxide to produce indoxyl. Oxidation of indoxyl produces indigo.

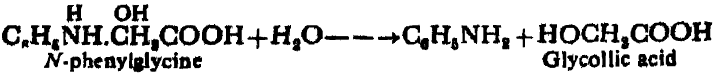


(*b*) **From Aniline.** By condensation of aniline with chloroacetic acid to get *N*-phenylglycine which is fused with caustic soda and sodamide at 570-570K (300-350°C) to produce indoxyl. This on oxidation gives indigo.



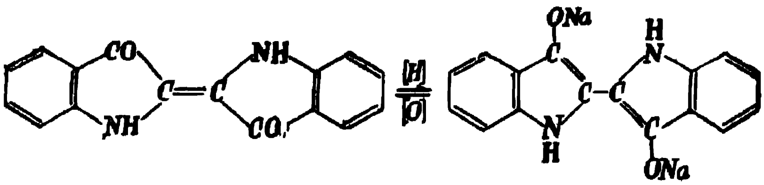
Function of sodamide is to remove water which will otherwise hydrolyse *N*-phenylglycine.

$$NaNH_2 + H_2O \longrightarrow NaOH + NH_3$$



$$\underset{N\text{-phenylglycine}}{C_6H_5\overset{H}{N}H.\overset{OH}{C}H_2COOH} + H_2O \longrightarrow C_6H_5NH_2 + \underset{\text{Glycollic acid}}{HOCH_2COOH}$$

Properties. Indigotin is a dark blue powder (m.p. 663 665K) having a coppered lustre. It can be sublimed under reduced pressure. It is insoluble in water but when its paste is agitated with sodium hyposulphite ($Na_2S_2O_4$) in large vats it is reduced to the soluble leuco-compound, *indigotin-white*.



Indigotin (*dark blue*) Indigotin-white (*colourless*)

For dyeing, the fabric is soaked in a solution of indigotin-white and then exposed to air. On standing in air indigotin-white is oxidised to indigotin and the fabric gets a dark blue colour which is extremely fast to washing and other colour-destroying agents. The shade of the colour is, however, dull and not very attractive.

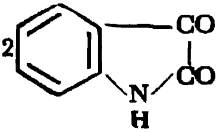
Structure of Indigotin

(*i*) Molecular formula of indigotin as deduced from its analytical data and molecular weight determination is $C_{16}H_{10}O_2N_2$.

(*ii*) Oxidation of indigotin with nitric acid gives two molecules of isatin and two oxygen atoms are added during oxidation.

$C_{16}H_{10}O_2N_2 + 2[O] \rightarrow 2C_8H_5O_2N$
Isatin

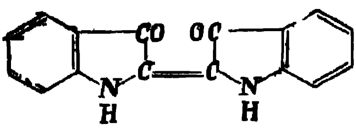
or 2



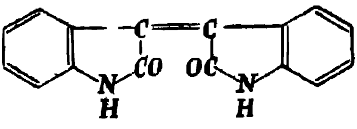
This suggests that in the indigotin molecule two identical units are joined together. On oxidation of indigotin, each one of these units gives a molecule of isatin.

(*iii*) Keeping the above facts in view there are three possible structures of indigotin as given below :

(*iv*) Indigotin was synthesised from isatin by Baeyer in 1878. Isatin on treatment with phosphorus pentachloride gives isatin

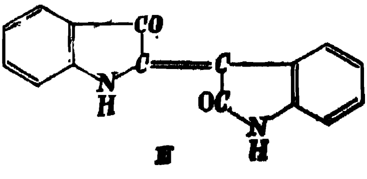


I ;



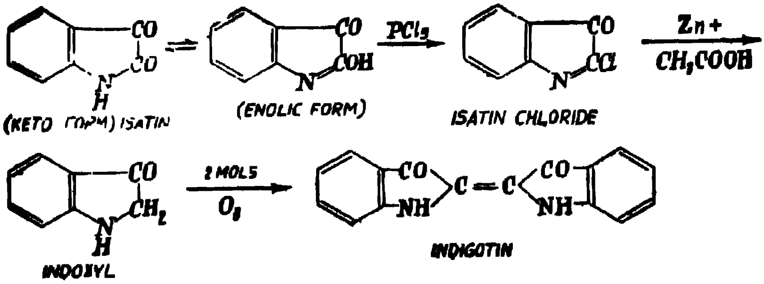
II

AND



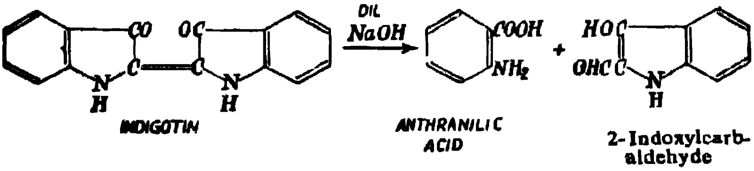
III

chloride which on reduction with zinc dust and glacial acetic acid yields indoxyl. This gives indigotin on atmospheric oxidation.

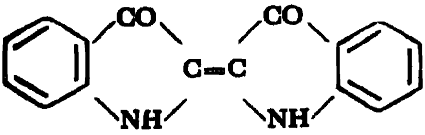


This shows that the formula I given above is the formula of indigotin.

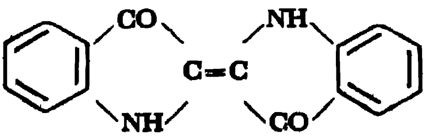
(v) This structure is further supported by the fact that indigotin on hydrolysis with dilute alkali gives anthranilic acid and 2-indoxylcarbaldehyde.



(vi) Due to the presence of carbon-carbon double bond two geometrical isomers are possible for indigotin as given below :



cis-form



trans-form

It has been found that the stable form of indigotin is the *trans*-form. There is, however, evidence showing that during dyeing the *cis*-form is first produced on the cloth but slowly changes into the stable *trans*-form

QUESTIONS

Essay Type :

1. Give the preparation and properties of (*i*) Indole ; (*ii*) Indoxyl ; and (*iii*) Isatin.

2. What are heterocyclic compounds ? How are they classified ? Discuss the methods of preparation and constitution of quinoline and isoquinoline.

3. Describe the reactions which helped the determination of the constitution of quinoline. Give its synthesis.

4. Establish the constitution of indigo and explain how it is used as a vat dye.

5. How is indigo isolated from the indigo plants ? Outline the steps leading to the present accepted structure of indigo.

6. Give an account of the synthetic manufacture of indigo.

(*Mysore B.Sc. 1972*)

Short Answer Type :

1. Explain why heterocyclic compounds exhibit aromatic properties.
(*Bangalore B.Sc. 1974*)

2. Write the structural formula of indigo. (*Bangalore B.Sc. 1974*)

3. Give the structures of the products in the following reactions :

(*a*) Quinoline $\xrightarrow{KMnO_4}$

(*b*) Isoquinoline $\xrightarrow{KMnO_4}$ (*Andhra B.Sc. 1974*)

4. Give the synthesis of Quinoline. (*Burdwan B.Sc. 1971*)

5. What happens when 1-Methylisoquinoline is treated with benzaldehyde and alkali ? (*Madras B.Sc. 1978*)

6. Write down the structures of quinoline and isoquinoline. How can a mixture of quinoline and isoquinoline be separated into its constituents ? What happens when these two compounds are oxidised ?
(*Delhi B.Sc. 1977 Supp.*)

7. How is quinoline obtained by Skraup's synthesis ?
(*Delhi B.Sc. Hons. 1979*)

5

Carbohydrates

1. **What Carbohydrates are ?**—Glucose, fructose, cane-sugar, starch and cellulose were all considered to be hydrates of carbon and were, therefore, named as *Carbohydrates.*

$C_6H_{12}O_6$ or $C_6(H_2O)_6$ Glucose or Fructose	$C_{12}H_{22}O_{11}$ or $C_{12}(H_2O)_{11}$ Sucrose or Maltose	$(C_6H_{10}O_5)_n$ or $[C_6(H_2O)_5]_n$ Starch or Cellulose

The term has, however, lost its significance as some carbohydrates cannot be represented as hydrates of carbon, *e.g.*, rhamnose $C_6H_{12}O_5$; rhamno-hexose, $C_7H_{14}O_6$ and some substances other than carbohydrates can be represented as hydrates of carbon, *e.g.*, acetic acid [CH_3COOH or $C_2(H_2O)_2$] and lactic acid [$C_3H_6O_3$ or $C_3(H_2O)_3$]. The name, however, is still retained. *The term carbohydrates now includes all polyhydroxy-aldehydes and ketones along with substances which yield these on hydrolysis.*

2. **Their Classification.**—Carbohydrates are classified as given below :

(1) **Monosaccharides**. These include non-hydrolysable sugars, *e.g.*, glucose and fructose, soluble in water and sweet in taste. These are building blocks of various carbohydrate molecules. They are polyhydric alcohols (containing five, six, seven or eight carbon atoms) as well as a carbonyl (an aldehydic or a ketonic) group. Those containing an aldehydic group are called aldoses while others containing a ketonic group are called ketoses. The number of carbon atoms in the molecule is indicated by a Greek prefix. For example :

$CH_2OH\ (CHOH)_4.CHO$, glucose is an aldohexose

while $CH_2OH.(CHOH)_3.COCH_2OH$, fructose is a ketohexose.

(2) **Oligosaccharides**. These are low-molecular-weight condensation polymers of monosaccharides containing two to nine monosaccharide units generally. These may be further classified as :

(*i*) **Disaccharides** (*containing two monosaccharide units*). Sugars like cane-sugar, maltose, lactose all having the formula $C_{12}H_{22}O_{11}$, one molecule of which on hydrolysis gives two monosaccharide molecules, are called disaccharides. These are crystalline solids, soluble in water and sweet in taste.

$$\underset{\text{Cane-sugar}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

(*ii*) **Trisaccharides** (*containing three monosaccharide units*). Sugars with general formula $C_{18}H_{32}O_{16}$, one molecule of which yields three monosaccharide molecules on hydrolysis are called trisaccharides, *e.g.*, raffinose.

(*iii*) **Similarly, we can have tetra-, penta-, and hexa-saccharides.**

(3) **Polysaccharides**. Non-sugars like starch, dextrin and cellulose, one molecule of which on hydrolysis yields a large number of monosaccharide molecules are called polysaccharides. These are amorphous, tasteless and mostly insoluble in water.

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} + nH_2O \longrightarrow \underset{\text{Glucose}}{nC_6H_{12}O_6}$$

These are further classified as :

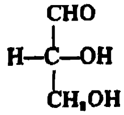
(*i*) *Homopolysaccharides* which on hydrolysis yield only one kind of sugar.

(*ii*) *Heteropolysaccharides* which on hydrolysis yield more than one kind of sugar.

MONOSACCHARIDES

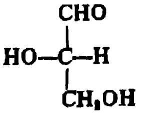
3. **The Monosaccharides.**—Monosaccharides include both aldoses and ketoses but the former are far more important than the latter. The simplest aldose is glycolaldehyde, $CH_2OH.CHO$ and lacks optical activity. Since all naturally occurring sugars are optically active, it will be more satisfactory to exclude this from the list of sugars. Monosaccharides may better be defined as *optically active polyhydroxy-aldehyeds or ketones*. A few individual aldoses are :

(*i*) *Aldotriose*, $C_3H_6O_3$. Glyceraldehyde, $CH_2OH.CHOH.CHO$ is an aldotriose. It contains one chiral carbon atom and exists in two optically active forms.



$$\begin{array}{c} CHO \\ | \\ H-C-OH \\ | \\ CH_2OH \end{array}$$

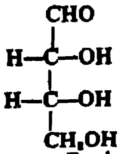
D-Glyceraldehyde



$$\begin{array}{c} CHO \\ | \\ HO-C-H \\ | \\ CH_2OH \end{array}$$

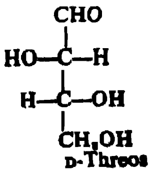
L-Glyceraldehyde

(*ii*) *Aldotetroses*, $CH_2OH.(CHOH)_2.CHO$. There are two chiral carbon atoms and it exists in four optically active forms*—D- and L-threose ; D- and L-erythrose.



$$\begin{array}{c} CHO \\ | \\ H-C-OH \\ | \\ H-C-OH \\ | \\ CH_2OH \end{array}$$

D-Erythrose



$$\begin{array}{c} CHO \\ | \\ HO-C-H \\ | \\ H-C-OH \\ | \\ CH_2OH \end{array}$$

D-Threose

(*iii*) *Aldopentoses*, $CH_2OH.(CHOH)_3.CHO$. There are three chiral carbon atoms in the molecule and it exists in eight optically active forms—D- and L-forms of ribose, arabinose, xylose and lyxose.

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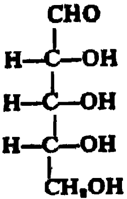
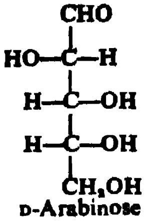
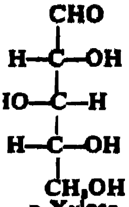
*For details of D and L notation refer to Part I, Chapter 10—Stereochemistry.



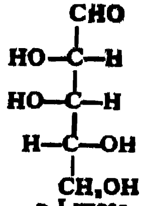
D-Ribose



D-Arabinose



D-Xylose



D-Lyxose

Aldopentoses resemble aldohexoses in properties but do not undergo fermentation.

(*iv*) *Aldohexoses*, $CH_2OH.(CHOH)_4.CHO$. There are four chiral carbon atoms in the molecule and it exists in sixteen optically active isomeric forms, *e.g.*, *glucose*, *mannose*, *galactose*, *allose*, *altrose*, *idose*, *gulose* and *talose* each existing in two forms related as the object and its mirror image. The two forms of each are designated as D- and L-forms.

Glucose is an important aldohexose and fructose is an important keto-hexose which we shall discuss in detail.

4. Glucose, Grape-sugar or Dextrose, $C_6H_{12}O_6$.—Glucose occurs in ripe grapes (hence the name grape-sugar), honey and most sweet fruits. It is a normal constituent of blood and is present in the urine of diabetic persons.

Preparation. (*i*) *From Sucrose.* Glucose can be easily prepared in the laboratory by the hydrolysis of an alcoholic solution of cane-sugar with a 4 per cent solution of hydrochloric acid in alcohol.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

Glucose being almost insoluble in alcohol crystallizes on cooling while fructose being comparatively more soluble remains in solution.

(*ii*) *From Starch.* Commercially pure glucose is manufactured by the hydrolysis of starch with dilute mineral acids.

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} + nH_2O \longrightarrow \underset{\text{Glucose}}{nC_6H_{12}O_6}$$

The starchy material is mixed with about three times its weight of water and dilute sulphuric acid (about 6N) and heated under pressure (4-5 atmospheres). When the hydrolysis is complete (the reaction mixture gives no colour with iodine), the excess of the acid is neutralized with calcium carbonate and filtered to remove calcium sulphate. The filtrate is decolorised with animal charcoal, concentrated in vacuum pans and crystallised when crystals of glucose monohydrate, $C_6H_{12}O_6.H_2O$ separate.

Although cellulose can be almost quantitatively hydrolysed to glucose but the process is lengthy and tedious. Glucose is, therefore, seldom manufactured by the hydrolysis of cellulose. It is, however, reported that in Russia they have been able to overcome various difficulties in the way of large-scale production of glucose from cellulose.

Properties : Physical. Glucose is a white crystalline solid (m.p. 419K) sweet in taste but is not as sweet as cane-sugar. It is sparingly soluble in alcohol and insoluble in ether but readily dissolves in water. It is optically active and is *dextro*-rotatory, hence the name *dextrose*. It has a specific rotation of +52·7°.

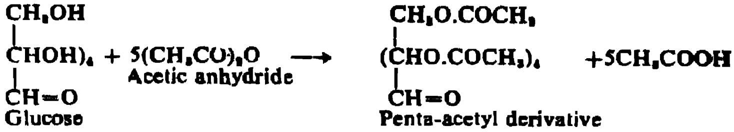
Chemical. Structural formula of glucose

$$CH_2OH-(CHOH)_4-CHO$$

indicates the presence of one aldehydic group, one primary alcoholic group and four secondary alcoholic groups. Chemical properties of glucose are, therefore, the properties of aldehyde and alcoholic groups present in its molecule. For example :

(*a*) **Reactions of the Hydroxyl group**

(*i*) *Acetylation*. Acetic anhydride reacts with the five —OH groups to give the penta-acetyl derivative of glucose.



$$\underset{\text{Glucose}}{\begin{matrix}CH_2OH\\ |\\ (CHOH)_4\\ |\\ CH{=}O\end{matrix}} + \underset{\text{Acetic anhydride}}{5(CH_3CO)_2O} \longrightarrow \underset{\text{Penta-acetyl derivative}}{\begin{matrix}CH_2O.COCH_3\\ |\\ (CHO.COCH_3)_4\\ |\\ CH{=}O\end{matrix}} + 5CH_3COOH$$

(*ii*) *Formation of Glucosides*. Glucose reacts with methanol in the presence of dry hydrochloric acid gas to form two methyl glucosides (ethers) designated as α- and β-glucosides. Isomers of the type of α- and β-glucosides are termed **anomers** while the carbon atom responsible for the existence of these anomers is called *anomeric carbon atom*.

$$\underset{\text{Glucose}}{C_6H_{11}O_5|\underline{OH}} \underline{\;+\;} \underset{\text{Methanol}}{\underline{H}|OCH_3} \xrightarrow{HCl} \underset{\substack{\text{Methyl glucosides}\\ (\alpha\text{- and }\beta\text{-})}}{C_6H_{11}O_5.OCH_3} + H_2O$$

These glucosides exhibit no aldehydic function and do not show mutarotation (*see* page 3·100).

(*iii*) *Formation of Glucosates*. With various metallic hydroxides glucose forms *glucosates*, *e.g.*, with calcium hydroxide it forms calcium glucosate, $C_6H_{11}O_6.CaO$ which is soluble in water. The structure of glucosates is still uncertain.

(*b*) **Reactions of the Aldehyde group**

(*i*) *Reduction*. When reduced with sodium amalgam and in aqueous solution, the aldehydic group is reduced to a primary alcoholic group to yield a hexahydric alcohol, *sorbitol*.

$$\underset{\text{Glucose}}{CH_2OH.(CHOH)_4.CHO} + 2[H] \rightarrow \underset{\text{Sorbitol}}{CH_2OH.(CHOH)_4CH_2OH} \quad (50\%)$$

High pressure catalytic reduction or electrolytic reduction in acid solution is better than reduction with sodium amalgam and water because in alkaline solution glucose tends to undergo rearrangement (*see* page 3·94).

Reduction of glucose with concentrated hydriodic acid and red phosphorus at 370K yields 2-iodohexane. Prolonged heating with conc. HI produces *n*-hexane.

$$CH_2OH.(CHOH)_4.CHO \xrightarrow{\text{Conc. HI}} \underset{\text{2-iodohexane}}{CH_3.(CH_2)_3.CHI.CH_3}$$

$$\xrightarrow[\text{with conc HI}]{\text{Prolonged heating}} \underset{n\text{-hexane}}{CH_3.CH_2.CH_2.CH_2.CH_2.CH_3}$$

(*ii*) *Oxidation*. With mild oxidising agents such as bromine water, glucose is oxidised to gluconic acid.

$$\underset{\text{Glucose}}{CH_2OH.(CHOH)_4.CHO}+[O] \xrightarrow{Br_2/H_2O} \underset{\text{Gluconic acid}}{CH_2OH.(CHOH)_4COOH} \ (50\%)$$

With strong oxidising agents like nitric acid, its terminal groups, $-CHO$ as well as $-CH_2OH$ are oxidised to $-COOH$ groups to give the dibasic acid, glucaric acid or glucosaccharic acid (often called *saccharic acid*). Some oxalic acid is also obtained.

$$\underset{\text{Glucose}}{CH_2OH.(CHOH)_4CHO}+3(O) \xrightarrow{HNO_3}$$

$$\underset{\text{Glucaric acid}}{COOH.(CHOH)_4.COOH}+H_2O \ (20\%)$$

Dicarboxylic acids obtained by oxidation of aldoses in general are known as *saccharic* or *aldaric acids*.

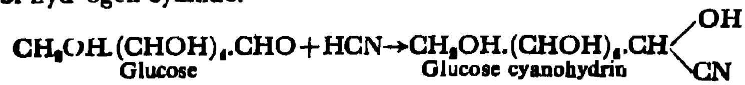
(*iii*) *Reducing Action*. Because glucose is readily oxidised, it acts as a strong reducing agent. It reduces Fehling's solution and ammoniacal silver nitrate.

$$\underset{\text{Glucose}}{CH_2OH.(CHOH)_4.CHO}+2Ag(NH_3)_2^+ + 2OH^-$$

$$\rightarrow \underset{\text{Gluconic acid}}{CH_2OH.(CHOH)_4.COOH}+2Ag+4NH_3+H_2O$$

It reduces more Fehling's solution than corresponds to one aldehyde group. This indicates that besides the aldehyde group other groups in the chain must be involved in this reduction.

(*iv*) *Addition Product with Hydrogen cyanide*. Glucose gives addition product, *glucose cyanohydrin* by the addition of a molecule of hydrogen cyanide.



$$\underset{\text{Glucose}}{CH_2OH.(CHOH)_4.CHO}+HCN \rightarrow \underset{\text{Glucose cyanohydrin}}{CH_2OH.(CHOH)_4.CH}{\begin{matrix} \diagup OH \\ \diagdown CN \end{matrix}}$$

Unlike other aldehydes glucose gives no addition product with sodium bisulphite and ammonia.

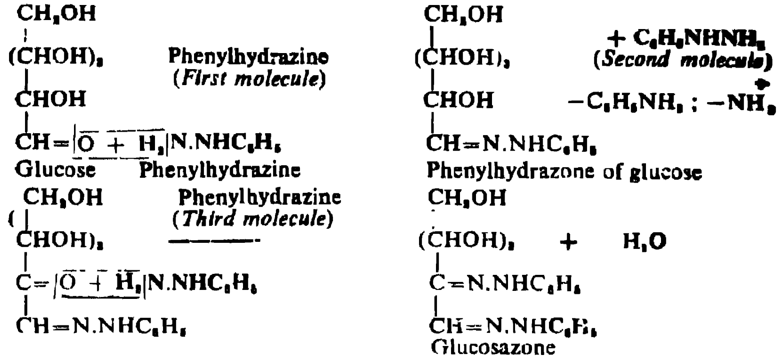
(*v*) *Action with Hydroxylamine*. Glucose condenses with hydroxylamine with the elimination of a molecule of water to yield the oxime.

$$\underset{\text{Glucose}}{CH_2OH(CHOH)_4CH=}\boxed{O \ + \ H_2}\underset{\text{Hydroxylamine}}{NOH}$$

$$\rightarrow \underset{\text{Glucose oxime}}{CH_2OH.(CHOH)_4.CH=NOH}+H_2O$$

(*vi*) *Action with Phenylhydrazine*. Glucose on treatment with excess of phenylhydrazine gives glucosazone. **Fischer** (1884-87) proposed the following mechanism of reactions involved in the formation of glucosazone.

Glucose reacts with one molecule of phenylhydrazine which condenses with the aldehyde group to give phenylhydrazone. When warmed with excess of phenylhydrazine, the secondary alcoholic group adjacent to the aldehyde group is oxidised by another molecule of phenylhydrazine, to a ketonic group. With this ketonic group, the third molecule of phenylhydrazine condenses to give glucosazone.

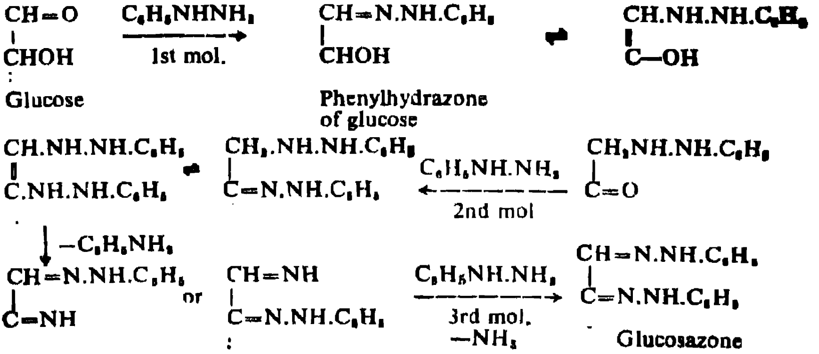

Phenylhydrazine (First molecule)
Glucose
Phenylhydrazine
$+ C_6H_5NHNH_2$ (Second molecule)
$-C_6H_5NH_2 ; -NH_3$
Phenylhydrazone of glucose
Phenylhydrazine (Third molecule)
$+ H_2O$
Glucosazone

Fischer's mechanism does not explain the following :

(*i*) How does phenylhydrazine which is a powerful reducing agent act as an oxidising agent in this case ?

(*ii*) Why should only two carbon atoms be involved in the osazone formation ?

Weygand (1940) suggested that osazone is produced as a result of *Amadori rearrangement* as given below :



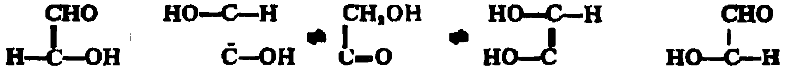
Herein we find that nowhere phenylhydrazine acts as an oxidising agent. This, however, does not explain why should only two carbon atoms be involved in the osazone formation.

(*c*) **Other Reactions :**

(*i*) ***Fermentation.*** Glucose is readily fermented by yeast to ethanol.

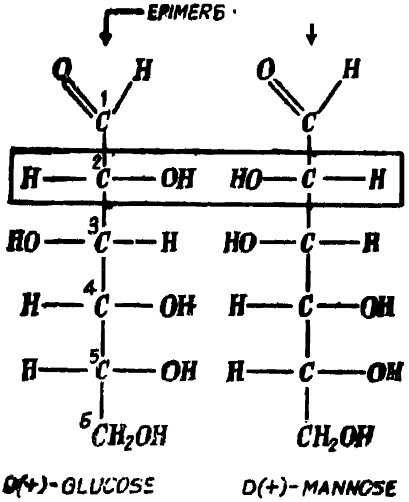
$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\text{Yeast}} \underset{\text{Ethanol}}{2C_2H_5OH} + 2CO_2$$

(*ii*) *Action of Alkalis.* When warmed with concentrated alkali, glucose first turns yellow, then brown and finally gives a resinous mass. A dilute solution of glucose, when warmed with dilute solution of alkali, gives a mixture of glucose, fructose and mannose. The same mixture is obtained if the starting material is fructose or mannose. This is called *Lobry de Bruyn Alberda van Ekenstein rearrangement* (1890) and is supposed to occur through 1 : 2-enolisation as shown below :



Glucose *trans*-diol Fructose *cis*-diol Mannose

D (+)-Glucose and D (+)-mannose are **epimers**. *Epimers are a pair of diastereomers that differ only in the configuration about a single carbon atom.*

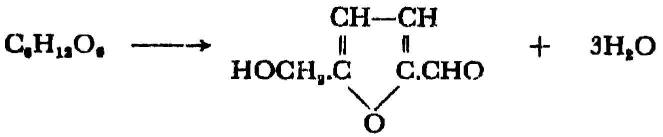


(*iii*) *Action of concentrated hydrochloric acid.* When heated with nc HCl glucose gives laevulic acid.

$$_6H_{12}O_6 \xrightarrow{\text{Conc HCl}} CH_3CO.CH_2.CH_2.COOH + HCOOH + H_2O$$

lucose Laevulic acid

On treatment with conc. HCl glucose can also give hydroxy-ethylfurfural.



Hydroxymethylfurfural

Hydroxmethylfurfural on acid treatment gives laevulic acid. is suggests that laevulic acid is produced from glucose *via* the mation of hydroxymethylfurfural as an intermediate compound.

Uses. (*i*) As a sweetening agent in confectionery.

(*ii*) In medicine and as food for children and invalids.

(*iii*) In fruit preservation and in making jams and jellies.

(*iv*) As a cheap reducing agent in industry and in the manufacture of wines.

(*v*) As a starting material in the synthesis of vitamin C.

Tests. (*i*) Heat some glucose in a dry test tube, it melts and then turns brown giving a burnt sugar smell.

(*ii*) Add concentrated sulphuric acid to glucose. Charring occurs only on heating the mixture.

(*iii*) Add Fehling's solution to glucose and warm, a red precipitate of cuprous oxide is obtained.

(*iv*) Heat glucose with ammoniacal silver nitrate solution, silver mirror is formed.

(*v*) To some glucose in a test tube add phenylhydrazine solution in acetic acid. Shake and heat the test-tube in a water bath. Fine yellow needles of glucosazone (m.p. 523K) separate.

(*vi*) **Molisch's test.** Add a few drops of alcoholic solution of α-naphthol to a solution of glucose. Slip about 1 cm^3 of concentrated sulphuric acid along the sides of the test-tube when a violet colour is obtained. *This test is given by all carbohydrates.*

5. Constitution of Glucose.

(*a*) MOLECULAR FORMULA. Molecular formula of glucose as determined from its analytical data and molecular weight determination is $C_6H_{12}O_6$.

(*b*) PRESENCE OF 5 —OH GROUPS. When treated with acetic anhydride, glucose gives the penta-acetate showing the presence of five hydroxyl groups. Since glucose is not easily dehydrated, *each hydroxyl group must be attached to a different carbon atom.*

(*c*) PRESENCE OF AN ALDEHYDIC GROUP.

(*i*) With HCN glucose gives cyanohydrin and with hydroxylamine it gives an oxime indicating the presence of a carbonyl group in glucose.

(*ii*) Glucose is oxidised with bromine water to gluconic acid, $C_6H_{12}O_7$—an acid with same number of carbon atoms. This shows that the carbonyl group present in glucose is an aldehydic group.

(*d*) CARBON ATOMS ARRANGED IN STRAIGHT CHAIN.

(*i*) On reduction with concentrated hydriodic acid and red phosphorus at 370K, glucose forms a mixture of 2-iodohexane and *n*-hexane. This indicates that the six carbon atoms in glucose are in a straight chain.

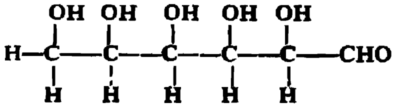
(*ii*) This conclusion is further supported by the fact that the polyhydroxy acid obtained from glucose by treatment with HCN followed by hydrolysis when reduced with hydriodic acid produces heptanoic acid, $CH_3.(CH_2)_5.COOH$—a straight-chain compound.

(*iii*) Aldehyde group being a monovalent group must be present at the end of the straight chain.

(*e*) OPEN-CHAIN STRUCTURE. Keeping the foregoing conclusions in view, Baeyer in 1870 suggested the following open-chain structural formula for glucose :

$$CH_2OH—CHOH—CHOH—CHOH—CHOH—CHO$$

There are four structurally different chiral carbon atoms (shown black in the structure given below) present in the molecule and it should, therefore, exist in $2^4=16$ optically active forms. All these are known and correspond to the D- and L-forms of *glucose*, *mannose*, *galactose*, *allose*, *altrose*, *gulose*, *idose* and *talose*.



$$H-\underset{H}{\overset{OH}{C}}-\underset{H}{\overset{OH}{C}}-\underset{H}{\overset{OH}{C}}-\underset{H}{\overset{OH}{C}}-\underset{H}{\overset{OH}{C}}-CHO$$

(*f*) EVIDENCE AGAINST OPEN-CHAIN STRUCTURE. This open-chain formula assigned to glucose readily accounts for most of the reactions satisfactorily but fails to explain the following :

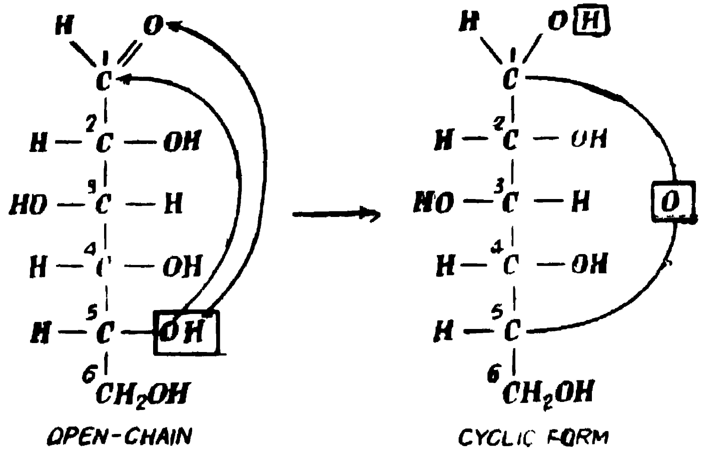
(*i*) Even though an aldehyde group is present in glucose, it does not react with $NaHSO_3$ and NH_3.

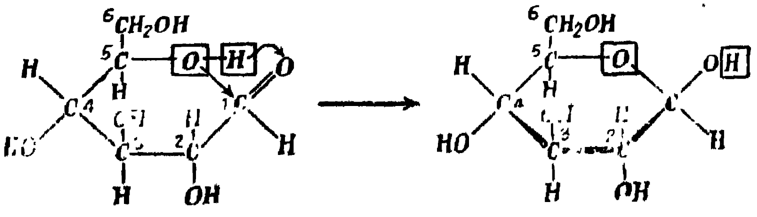
(*ii*) Two stereoisomeric forms of glucose (α- and β-glucose) exist. α-Glucose with specific rotation +110° is obtained by crystallizing glucose from alcoholic or acetic acid solution whereas β-glucose with specific rotation +19·7° is obtained by crystallizing glucose from pyridine solution.

(*iii*) An aqueous solution of glucose shows *mutarotation*, *i.e.*, its specific rotation gradually falls from +110° to +52·5° in case of α-glucose and increases from +19·7° to +52·5° in case of β-glucose.

(*iv*) Two isomeric methyl glucosides (α- and β-) are obtained by heating glucose with methyl alcohol and dry HCl gas.

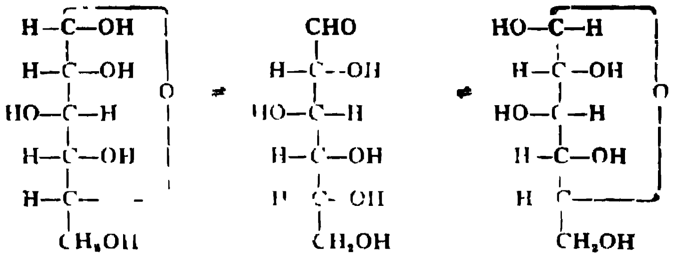
(*g*) RING STRUCTURE. To account for the above facts satisfactorily, Tollen suggested in 1883 a ring formula for glucose. He





assumed a butylene oxide ring (five-member ring containing oxygen atom) for glucose.

Later work by Haworth, Hirst and their co-workers (1926 onwards) has shown it to be a six-member amylene oxide ring. The ring formula can have two different structures related to each other as the object and its mirror image and which represent the two stereoisomeric forms of glucose—α- and β-glucose. The two stereoisomeric ring forms of a sugar are referred to as anomers.



α-Glucose $[\alpha]_D = +110°$ — Possible intermediate form — β-Glucose $[\alpha]_D = +19·7°$

The ring structure explains all the reactions of glucose. The objections against the open-chain structure of glucose have also been satisfactorily explained. For example,

(*i*) *Existence of α- and β-glucose.* The aldehydic carbon atom (shown in black type) becomes chiral on ring formation and gives rise to two anomers α- and β-glucose.

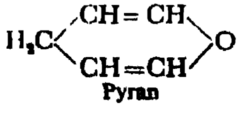
(*ii*) *Existence of two anomeric methylglucosides.* Corresponding to α- and β-glucose explained above, we have two stereoisomeric glucosides—α- and β-methylglucosides.

(*iii*) *No reaction with $NaHSO_3$ and NH_3.* The glucose ring is not very stable. It is easily broken up by strong reagents like HCN, NH_2OH, $NH_2.NH.C_6H_5$, etc., to give the intermediate aldehyde form which reacts with them just like an aldehyde.

Weak reagents like NH_3 and $NaHSO_3$ are unable to open the chain and cannot react with it. This explains the inability of glucose to form aldehyde-ammonia and bisulphite compound.

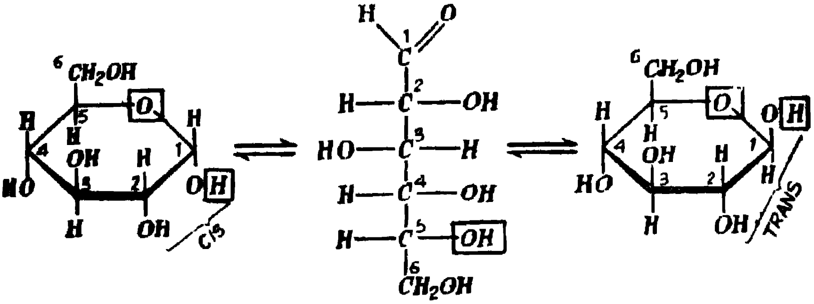
(*iv*) *It explains mutarotation.* Ordinary glucose is α-glucose with specific rotation +110°. In solution α-glucose slowly changes into an equilibrium mixture of α-glucose (38%) and β-glucose (62%) and mixture has specific rotation 52·5°. Similarly, a solution of β-glucose (specific rotation = +19·7°) on standing changes into the same equilibrium mixture (specific rotation = 52·5°). The phenomenon is termed *Mutarotation.*

(*h*) PYRANOSE STRUCTURE FOR GLUCOSE. Haworth (1926) proposed a hexagonal formula for glucose based on the heterocyclic compound pyran having a six-member ring with oxygen as one of the atoms.



Pyran

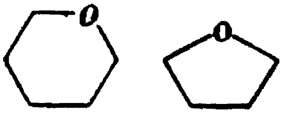
The *pyranose structure* is applicable to nearly all sugars and is supported by X-ray analysis. Pyranose structure for the two stereoisomers α- and β-glucose are given below :



α-D(+)-GLUCOSE D(+)-GLUCOSE β-D(+)-GLUCOSE

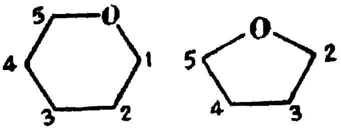
How to write Haworth structures ? Haworth structures can be written from the Fischer projection in the following steps ;

1. Draw a tetrahydropyran (a) or tetrahydrofuran (b) ring as required.



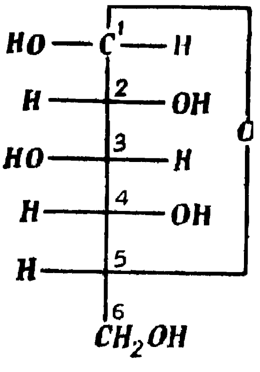
(a) (b)

2. Number the ring carbons starting with the anomeric C as 1 (this will be the first C after the ring O), moving clockwise, around the ring. In a furanose ring, however, this will not be C_1.

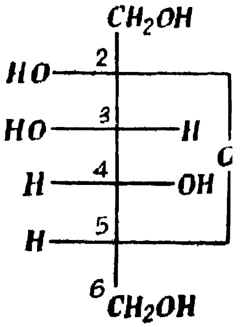


(a) (b)

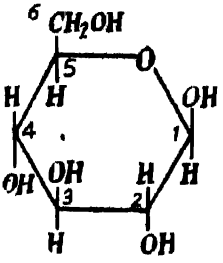
3. Draw vertical bonds through each ring C and attach substituents. Any terminal $-CH_2OH$ (or other group attached below the last ring C) is shown pointing up. All other atoms or groups on the left of Fischer projection are shown pointing up while those on the right are shown pointing down as illustrated below in the case of β-D-glucopyranose and β-D-fructofuranose.



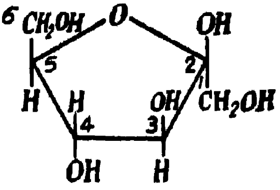
(*Fischer projection*)
β-D-glucopyranose



(*Fischer projection*)
β-D-fructofuranose

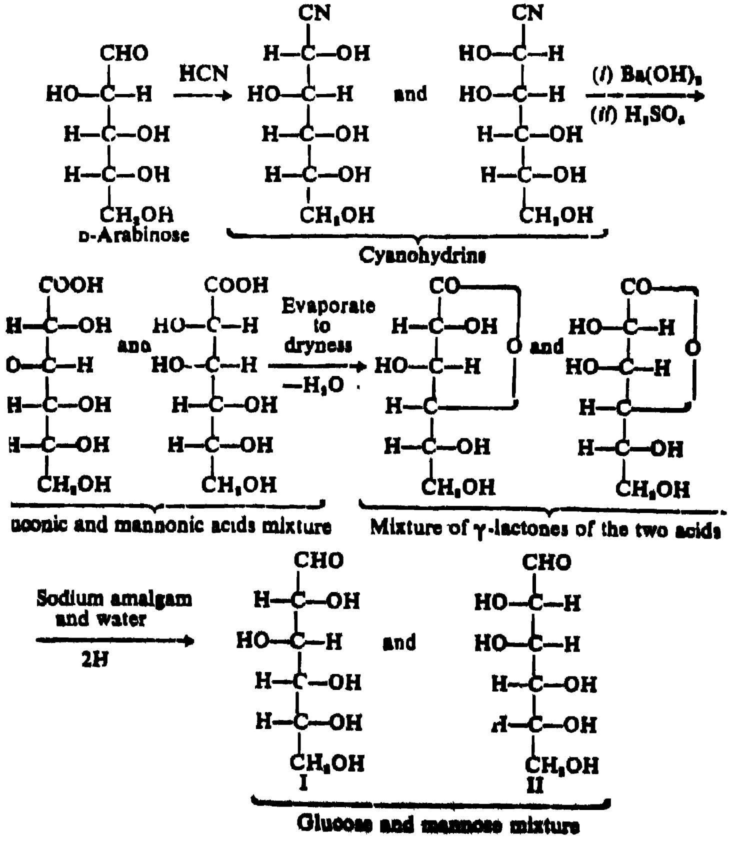


(*Haworth structure*)
β-D-glucopyranose



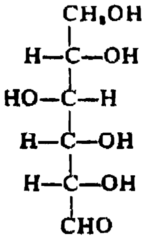
(*Haworth structure*)
β-D-fructofuranose

6. **Configuration of Glucose.**—The configuration (*arrangement of hydrogen atoms and hydroxyl groups in space*) follows from that of the arabinose. By Kiliani's synthesis arabinose is converted into glucose and mannose as given in the following equations where open-chain formulae are written for simplicity sake.



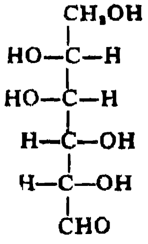
Accepting the configuration as given above, the configuration of glucose is either **I** or **II**. Glucose forms on oxidation with dilute nitric acid, glucaric acid, $COOH.(CHOH)_4.COOH$. Another sugar gulose also yields glucaric acid on oxidation. This shows that glucose and gulose differ only in their terminal groups —CHO and $-CH_2OH$ which are interchanged in them ; the configuration of the rest of carbon atoms is identical.

Thus out of the configurations **I** and **II**, the one which gives rise to a new sugar, when the terminal groups are interchanged, is the configuration of glucose. By writing configurations after interchanging the terminal groups, we find the formulae **III** and **IV** as obtained from **I** and **II** respectively.



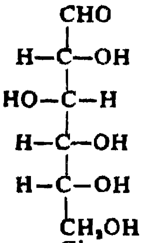
III

and

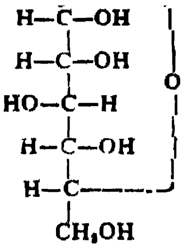


IV

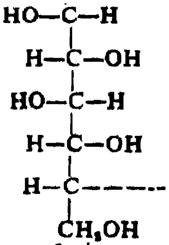
It can be seen by rotating the formulae in the plane of the paper that formulae **II** and **IV** are identical while **I** and **III** are different. Hence configuration of glucose is given by the formula **I**, that of gulose by **III** and of mannose by **II**. The accepted configuration of glucose is, therefore, represented by the following formulae :



Glucose



α-glucose



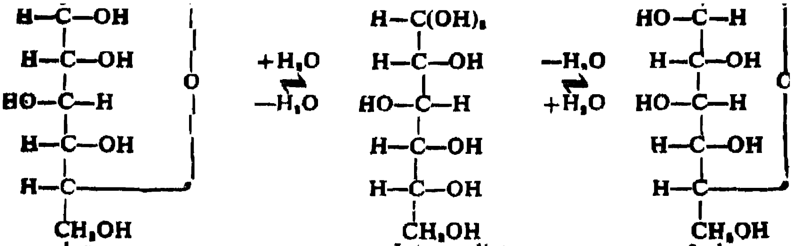
β-glucose

7. **Mutarotation.**— Glucose is dextro-rotatory, the specific rotation of freshly prepared aqueous solution of glucose crystallized from alcoholic or acetic acid solution decreases gradually from +110° to +52·56° in about 24 hours. The change is accelerated by heat or the presence of an alkali. Similarly, specific rotation of a freshly prepared aqueous solution of glucose crystallized from pyridine solution increases from +19·7° to +52·56°. The phenomenon, first discovered by *Dubrunfant* in 1846, is very common and is exhibited by various optically active compounds especially sugars.

***The change in specific rotation of an optically active solution without any change in other properties is known as* mutarotation.**

Mutarotation has been explained by assuming that glucose exists in two forms, anomeric α- and β-varieties. Glucose obtained from alcoholic or acetic acid solution is the α- form with specific rotation $[\alpha]_D = +110°$ while glucose obtained from pyridine solution is the β-variety with specific rotation $[\alpha]_D = +19{\cdot}7°$. In an aqueous solution the two varieties are present as an equilibrium mixture containing about 37% α- and 63% of β-variety and formed by isomerisation of α-form into the β-form and *vice versa*.

Mechanism of Mutarotation. According to Lowry (1925), mutarotation is possible only in the presence of a solvent like water which can act both as an acid and a base. It appears that when mutarotation takes place the ring opens and then recloses in the inverted position or in the original position. Lowry proposed that in water the transformation occurred through the intermediate product *aldehydrol.*



α-glucose $[\alpha]_D = +110°$

Intermediate aldehydrol form

β-glucose $[\alpha]_D = +19{\cdot}7°$

$[\alpha]_D$ for an equilibrium mixture of the α-(37%) and β-(63%) varieties $= +52{\cdot}56°$

Table 49·1. Specific rotations of some mono and disaccharides

Sugar	*Specific rotation (ρ)*		
	α	β	*Equilibrium mixture*
Glucose	+110	+19·7	+52·56
Fructose	−21	−133	−92
Mannose	+30	−17	+14
Lactose	+90	+35	+55
Maltose	+168	+112	+136

8. Fructose, Fruit Sugar or Laevulose, $C_6H_{12}O_6$ – Fructose is the most important ketose. It is found in fruits and honey.

Preparation of Fructose.

(*i*) *From Cane-sugar.* Fructose is prepared by the hydrolysis of a concentrated solution of cane-sugar with dilute hydrochloric acid or sulphuric acid.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

Fructose is separated from the mixture after the hydrolysis is complete by treating it with lime when calcium fructosate, $C_6H_{12}O_6$. CaO is precipitated while calcium glucosate remains in solution. The precipitate is separated, suspended in water and treated with carbon dioxide when calcium carbonate is precipitated and fructose is left in solution. The solution is concentrated to crystallize fructose.

$$\underset{\text{Calcium fructosate}}{C_6H_{12}O_6.CaO} + CO_2 \longrightarrow \underset{\text{Fructose}}{C_6H_{12}O_6} + \underset{\text{ppt.}}{CaCO_3}$$

(*ii*) ***From Inulin.*** Fructose is manufactured by the hydrolysis of inulin (a polysaccharide which occurs in dahlia tubers and Jerusalem artichokes) with dilute sulphuric acid.

$$\underset{\text{Inulin}}{(C_6H_{10}O_5)_n} + nH_2O \longrightarrow \underset{\text{Fructose}}{nC_6H_{12}O_6}$$

The excess of sulphuric acid is precipitated with barium carbonate and the solution concentrated when fructose crystallizes out.

Properties : Physical. Fructose is a white crystalline solid (m.p. 375K with decomposition). It is sweet in taste and is $1\frac{3}{4}$ times as sweet as cane-sugar. It is the sweetest of all sugars. It is readily soluble in water but is sparingly soluble in alcohol and insoluble in ether. It is laevorotatory and is, therefore, called *laevulose*.

Like glucose it shows mutarotation and the specific rotation of α-fructose is $-21°$, that of β-fructose is $-133°$. Specific rotation of the equilibrium mixture obtained on standing is $-92°$.

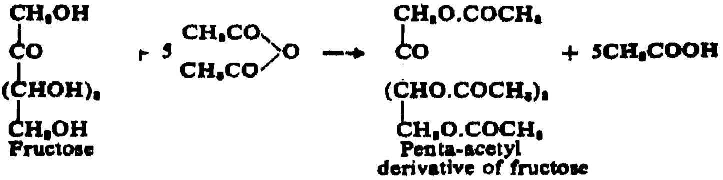
Chemical. Structural formula of fructose

$$CH_2OH.CO.(CHOH)_3.CH_2OH$$

indicates the presence of one ketonic group, two primary and three secondary alcoholic groups. Chemical properties of fructose are, therefore, the properties of these groups as given below :

(*a*) **Reactions of the Hydroxyl groups :**

(*i*) ***Acetylation.*** Acetic anhydride reacts with the five hydroxyl groups to form the penta-acetyl derivative of fructose.



$$\begin{array}{l}CH_2OH\\ |\\ CO\\ |\\ (CHOH)_3\\ |\\ CH_2OH\\ \text{Fructose}\end{array} + 5\left.\begin{array}{l}CH_3CO\\ CH_3CO\end{array}\right\rangle O \longrightarrow \begin{array}{l}CH_2O.COCH_3\\ |\\ CO\\ |\\ (CHO.COCH_3)_3\\ |\\ CH_2O.COCH_3\\ \text{Penta-acetyl}\\ \text{derivative of fructose}\end{array} + 5CH_3COOH$$

(*ii*) ***Formation of Fructosides.*** When treated with monohydric alcohols in presence of dry hydrochloric acid gas, fructose gives *fructosides*.

$$\underset{\text{Fructose}}{C_6H_{11}O_5}\boxed{OH + H}\underset{\text{Ethanol}}{OC_2H_5} \xrightarrow{HCl} \underset{\text{Ethyl fructoside}}{C_6H_{11}O_5\text{—}OC_2H_5} + H_2O$$

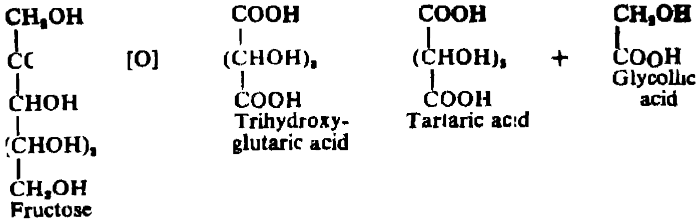
(*iii*) *Formation of Fructosides.* With various metallic hydroxides fructose forms fructosates, *e.g.*, with calcium hydroxide it forms calcium fructosate, $C_6H_{12}O_6.CaO$ which is insoluble in water.

(*b*) **Reactions of the Ketonic group** :

(*i*) *Reduction.* When reduced with sodium amalgam and water or catalytically, or electrolytically, fructose gives a mixture of sorbitol and mannitol—two optical isomerides.

$$\underset{\text{Fructose}}{CH_2OH.CO(CHOH)_3CH_2OH} \xrightarrow{[H]} \underset{\text{Mixture of Sorbitol and Mannitol}}{CH_2OH.(CHOH)_4.CH_2OH}$$

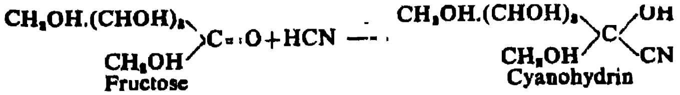
(*ii*) *Oxidation.* Fructose is not oxidised by bromine water. A strong oxidising agent like nitric acid oxidises fructose to a mixture of trihydroxyglutaric, tartaric and glycollic acids.



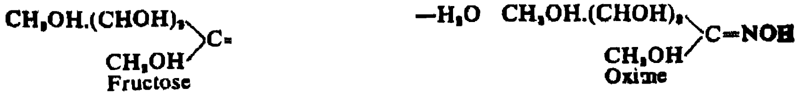
(*iii*) *Reducing Action.* Like glucose, fructose is also a strong reducing agent. It reduces both Fehling's solution and ammoniacal silver nitrate. Fructose reduces Fehling's solution even though it contains a ketonic group (rather than an aldehyde group). This can be explained as due to the formation of glucose from fructose by enolisation.

The alkaline reaction conditions facilitate the formation of an equilibrium mixture of keto and enol forms of the open chain structure (see page 3·34—action of alkalis). Enolisation results in the formation of glucose from fructose or *vice versa.*

(*iv*) *Addition product with Hydrogen cyanide.* Fructose forms a cyanohydrin with hydrogen cyanide.

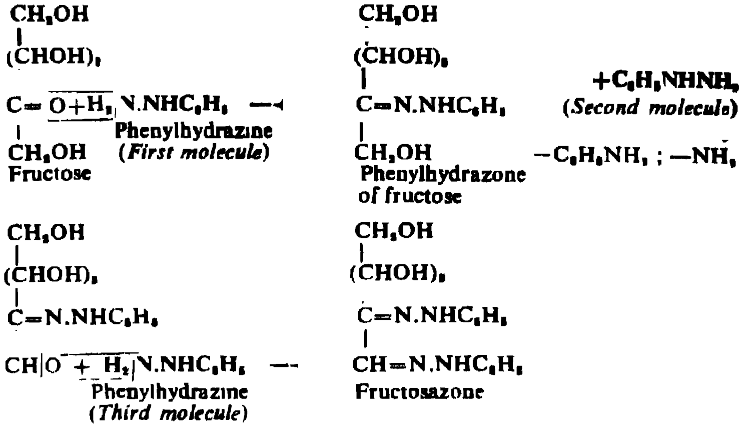


(*v*) *Action with Hydroxylamine.* Fructose reacts with hydroxylamine to form the oxime.



(*vi*) *Action of Phenylhydrazine.* Fructose is condensed with phenylhydrazine to give phenylhydrazone. With excess of phenylhydrazine it gives fructosazone. Fischer (1884-87) proposed the following mechanism for the formation of osazone.

When heated with excess of phenylhydrazine, the phenylhydrazone first produced is oxidised. The primary alcoholic group originally adjacent to the ketonic group is changed to the aldehyde group. This finally reacts with another molecule of phenylhydrazine to yield fructosazone (*cf.* glucosazone).

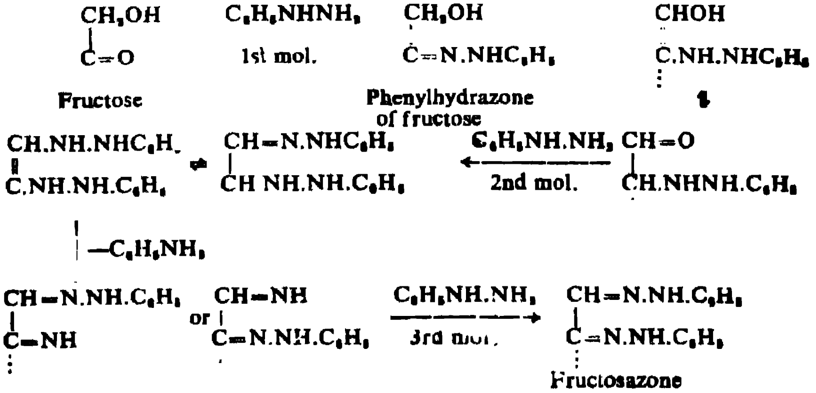


Fischer mechanism does not explain the following :

(*i*) How does phenylhydrazine, which is a powerful reducing agent, act as an oxidising agent in this case ?

(*ii*) Why should only two carbon atoms be involved in the osazone formation ?

Weygand (1940) suggested that osazone is produced as a result of Amadori rearrangement as given below :



It should be noted that even the Weygand mechanism does not explain why only the first two carbon atoms be involved in osazone formation.

(*c*) **Other Reactions** :

(*i*) ***Fermentation***. Fructose is fermented by yeast to ethyl alcohol.

$$\underset{\text{Fructose}}{C_6H_{12}O_6} \xrightarrow{\text{Yeast}} \underset{\text{Ethanol}}{2C_2H_5OH} + 2CO_2$$

(*ii*) *Action of Alkalis.* Fructose does not form a resin with alkalis. When warmed with dilute alkali, a mixture of glucose, fructose and mannose is obtained. This is called *Lobry de Bruyn Alberda van Ekenstein rearrangement. For mechanism see* page 3·94.

(*iii*) *Action of concentrated hydrochloric acid.* When heated with conc. HCl fructose gives laevulic acid. The yield is better than from glucose.

$$\underset{\text{Fructose}}{C_6H_{12}O_6} \xrightarrow{\text{Conc. HCl}} \underset{\text{Laevulic acid}}{CH_3CO.CH_2.CH_2.COOH} + HCOOH + H_2O$$

Tests. (*i*) Add concentrated sulphuric acid to fructose. A brown colour is formed in cold which changes to black on heating.

(*ii*) **Pinoff's test.** Heat a solution of fructose with ammonium molybdate and a few drops of acetic acid. A blue coloration is obtained.

(*iii*) **Selivanoff's test.** To fructose add a dilute solution of resorcinol in dilute hydrochloric acid. A deep reddish-brown precipitate soluble in alcohol is obtained. *This test is used to distinguish it from glucose,* which gives only slightly pink colour.

(*iv*) Tests with Fehling's solution and ammoniacal silver nitrate are similar to those for glucose (*see* page 3·95).

(*v*) **Furfural test.** To a dilute solution of fructose (1 cm^3) add 1% alcoholic solution of α-naphthol (1 cm^3) and then about 6 cm^3 of hydrochloric acid. A violet colour will be obtained on boiling the mixture. *This is another test used for distinction between glucose and fructose*

Uses. Fructose finds use as sweetening agent and is used by diabetic patients in place of cane-sugar.

9. Comparison between Glucose and Fructose.

Points of Similarity :

(*i*) Both give penta-acetyl derivatives with acetic anhydride.

(*ii*) With alcohols both give similar products—glucose gives glucoside and fructose gives fructoside.

(*iii*) With hydrogen cyanide both give cyanohydrins.

(*iv*) With hydroxylamine both give similar oximes.

(*v*) With phenylhydrazine both give similar osazones.

(*vi*) Both are strong reducing agents and reduce Fehling's solution and ammoniacal silver nitrate.

(*vii*) Both on fermentation with yeast give ethanol.

(*viii*) When warmed with dilute alkali solution, both yield a mixture of glucose, fructose and mannose.

(*ix*) Both give laevulic acid when heated with concentrated hydrochloric acid.

Points of Difference :

(*i*) Glucose is *dextro*-rotatory whereas fructose is *laevo*-rotatory

(*ii*) Glucose on reduction gives sorbitol while fructose gives a mixture of sorbitol and mannitol with sodium amalgam and water.

(*iii*) Glucose on oxidation with nitric acid gives gluconic and glucaric acids but fructose gives a mixture of trihydroxyglutaric, tartaric and glycollic acids.

(*iv*) With concentrated alkali, glucose gives a resinous mass, fructose does not.

(*v*) With lime glucose gives calcium glucosate (soluble in water) whereas fructose gives calcium fructosate which is insoluble in water.

10. Constitution of Fructose.

(*a*) MOLECULAR FORMULA. Molecular formula of fructose as determined from its analytical data and molecular weight determination is $C_6H_{12}O_6$.

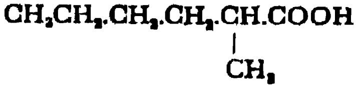
(*b*) PRESENCE OF 5 —OH GROUPS. When treated with acetic anhydride, fructose gives the penta-acetate showing the presence of five hydroxyl groups. Since fructose is not easily dehydrated, *each hydroxyl group must be attached to a different carbon atom*.

(*c*) PRESENCE AND POSITION OF A KETONIC GROUP.

(*i*) With HCN fructose gives a cyanohydrin and with hydroxylamine it gives an oxime indicating the presence of a carbonyl group.

(*ii*) When oxidised with nitric acid, fructose is converted into a mixture of trihydroxyglutaric, tartaric and glycollic acid. Since each one of these acids contains fewer carbon atoms than the fructose, the carbonyl group in fructose must be a ketonic group.

(*iii*) On hydrolysing the cyanohydrin of fructose and reducing the product with hydriodic acid we get 2-methylhexanoic acid.



$$CH_3CH_2.CH_2.CH_2.\underset{\underset{CH_3}{|}}{CH}.COOH$$

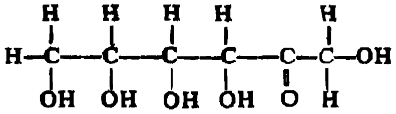
This shows that the ketonic group in fructose is present adjacent to one of the terminal carbon atoms.

(*d*) CARBON ATOMS ARRANGED IN STRAIGHT CHAIN. Fructose on reduction gives a mixture—sorbitol and mannitol. These on reduction with conc. HI and red phosphorus at 370K give a mixture of 2-iodohexane and *n*-hexane. This indicates that the six carbon atoms in fructose are arranged in a straight chain.

(*e*) OPEN-CHAIN STRUCTURE. Keeping the foregoing conclusion in view, the structural formula that can be assigned to fructose is

$$CH_2OH—CHOH—CHOH—CHOH—CO—CH_2OH$$

The formula contains three structurally different chiral carbon atoms (shown black in the formula given below) and can, therefore, exist in 2^3=eight optically active forms. Of these six are known.



$$H-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-\underset{\|O}{C}-\underset{H}{\overset{H}{C}}-OH$$

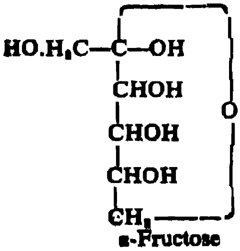
(*f*) EVIDENCE AGAINST OPEN-CHAIN STRUCTURE. This open-chain structure assigned to fructose readily accounts for most of the reactions satisfactorily but fails to explain the following :

(*i*) Even though a ketonic group is present, it does not react with $NaHSO_3$.

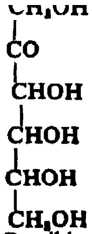
(*ii*) An aqueous solution of fructose shows mutarotation which suggests that it exists in two forms.

(*iii*) Two stereoisomeric methyl fructosides are known.

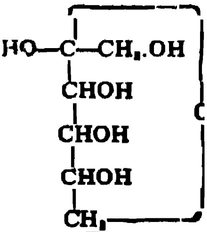
(*g*) RING STRUCTURE. To explain the above objections satisfactorily ring formula is proposed for fructose just as in the case of glucose. Thus α- and β-fructose are represented as :



α-Fructose



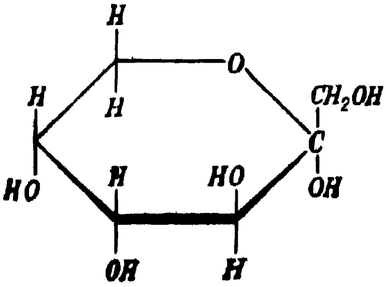
Possible intermediate open-chain form



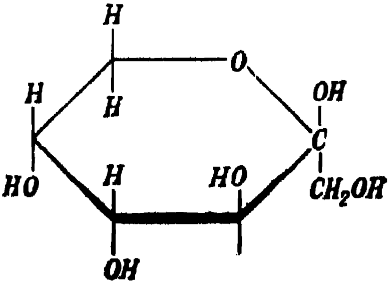
β-Fructose

Various objections against the open-chain structure can be explained on the basis of ring structure as in the case of glucose.

(*h*) PYRANOSE STRUCTURE FOR FRUCTOSE. The hexagonal formula for fructose based on pyrane ring is gien below :

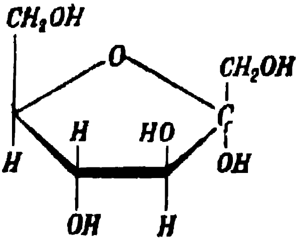


α-Fructopyranose

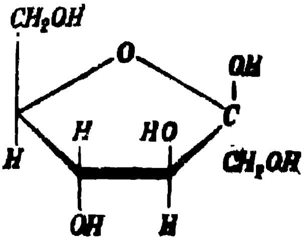


β-Fructopyranose

Fructose is also known to exist in γ-form called α- and β-fructofuranose having a five-member oxide ring. Sucrose molecule is made up of one glucose molecule and one fructose molecule. This fructose molecule in sucrose is γ-fructose. The structure as well as the configuration of γ-fructose is represented as follows :

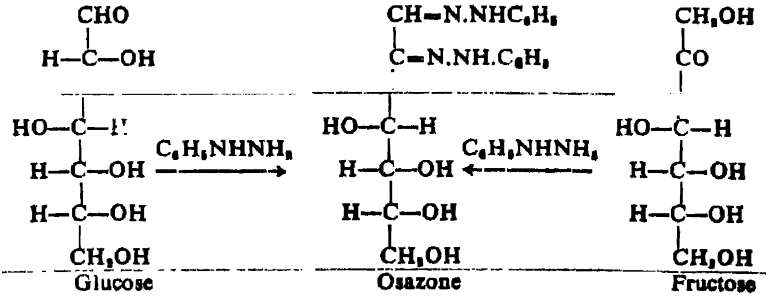


α-Fructofuranose



β-Fructofuranose

11. **Configuration of Fructose.**—Glucose and fructose both give the same osazone. Further since osazone formation involves only the first two carbon atoms, it follows that the configuration of the rest of the molecule in glucose and fructose must be the same. Knowing the configuration of glucose we write the configuration of fructose



$$\begin{array}{ccccc}
\text{CHO} & & \text{CH=N.NHC}_6\text{H}_5 & & \text{CH}_2\text{OH} \\
\text{H—C—OH} & & \text{C=N.NH.C}_6\text{H}_5 & & \text{CO} \\
\text{HO—C—H} & & \text{HO—C—H} & & \text{HO—C—H} \\
\text{H—C—OH} & \xrightarrow{C_6H_5NHNH_2} & \text{H—C—OH} & \xleftarrow{C_6H_5NHNH_2} & \text{H—C—OH} \\
\text{H—C—OH} & & \text{H—C—OH} & & \text{H—C—OH} \\
\text{CH}_2\text{OH} & & \text{CH}_2\text{OH} & & \text{CH}_2\text{OH} \\
\text{Glucose} & & \text{Osazone} & & \text{Fructose}
\end{array}$$

(*Parts with identical configuration are enclosed within line.*)

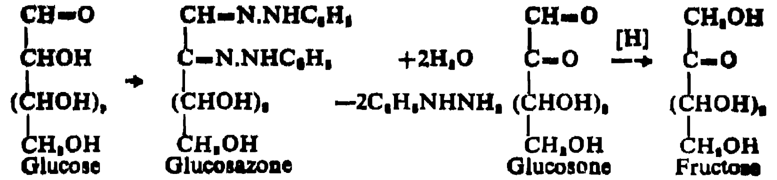
12. **Some Typical Conversions in Monosaccharides.**—Knowing the general reactions of monosaccharides we can devise schemes for the mutual transformations as shown in the examples given below :

(*a*) **Conversion of Glucose into Fructose.** It is carried out in the following steps :

(*i*) Glucose is warmed with phenylhydrazine (*excess*) when it gives glucosazone (*see* page 3·93).

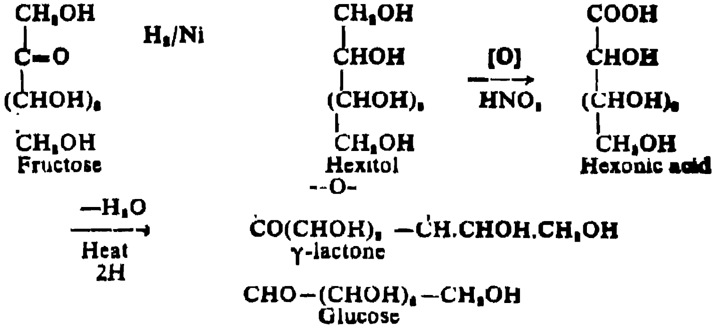
(*ii*) Glucosazone is treated with dilute hydrochloric acid when it gives glucosone by hydrolysis.

(*iii*) The latter on reduction with zinc dust and acetic acid gives fructose (an aldehyde group is reduced more readily than ketonic group).



These are general steps and can be used for converting any aldose into its corresponding ketose.

(*b*) **Conversion of Fructose into Glucose.** Fructose on catalytic reduction gives hexitol (a mixture of sorbitol and mannitol) which on oxidation gives hexonic acid (a mixture of gluconic acid and mannonic acid). This loses water on heating to give a γ-lactone which is subsequently reduced with sodium amalgam in faintly acid solution to glucose.

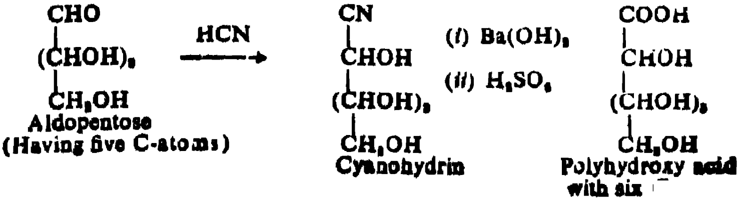


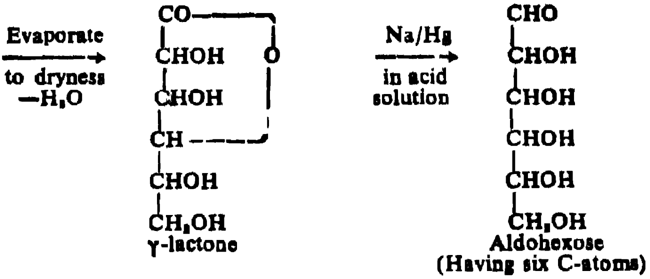
Making use of these steps we can convert any ketose into its corresponding aldose.

(*c*) **Conversion of an Aldose into the next higher Aldose** (***Ascending the sugar series***). An aldose (say, aldopentose) may be converted into its next higher member (aldohexose here) by means of **Kiliani reaction** (1886).

(*i*) The aldopentose is dissolved in dilute HCN and the cyanohydrin obtained is hydrolysed with aqueous barium hydroxide. The mixture is acidified with a calculated quantity of dilute sulphuric acid and barium sulphate precipitate is filtered off. A polyhydroxy acid with six carbon atoms is obtained in aqueous solution.

(*ii*) The solution is evaporated to dryness when γ-lactone is obtained. This on reduction with sodium amalgam in faintly acid solution yields an aldohexose.

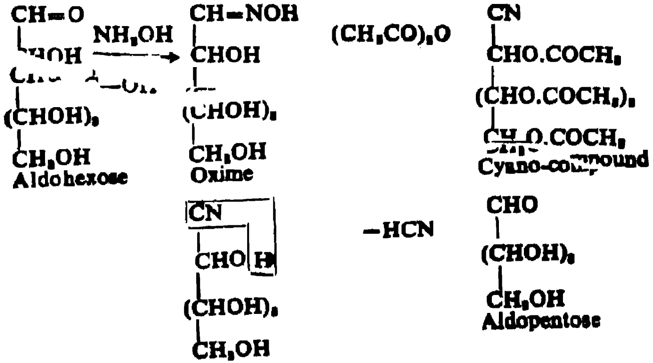




(*d*) **Conversion of an Aldose into the next lower Aldose** (*Descending the sugar series*). An aldose (say, aldohexose) is converted into its next lower aldose (aldopentose here) by **Wohl's method** (1893) given below :

(*i*) The aldohexose is treated with hydroxylamine and the oxime produced is heated with acetic anhydride. In this way the oxime is dehydrated to the cyano-compound whereas the hydroxyl groups get acetylated.

(*ii*) The acetyl derivative is warmed with ammoniacal silver nitrate which removes the acetyl groups by hydrolysis and eliminates a molecule of HCN. An aldopentose is obtained as a result of these changes.



DISACCHARIDES

13. **Sucrose, Cane-sugar or Beet-sugar, $C_{12}H_{22}O_{11}$.**—Sucrose is one of the most important compounds commercially. Cane-sugar has been known from early days and its crude form was separated from cane-juice. India has been the chief producer of cane-sugar from time immemorial. Later on, other countries like Java, Cuba, Philippines, etc., also started producing sugar and they contributed towards the development of better techniques for the production of refined sugar.

Its main sources are sugarcane and beet. In cold countries like Russia where beet is in abundance, it is extracted from beet. In tropical countries like India it is mostly obtained from sugarcane.

Lower part of the sugarcane is sweeter as compared with the upper part while the percentage of sugar content varies with the quality of cane in different localities. Indian sugarcane contains about 12-13% of sugar while it is about 19% in the sugarcane grown in Java.

14. Manufacture of Sucrose.—The process of manufacture of cane-sugar as followed in India involves the following steps :

(1) **Extraction of the juice.** Sugarcane is thoroughly cleaned and cut into short lengths soon after it is cut, to avoid fermentation which causes inversion of sucrose present into non-crystallizable sugars. These cane pieces are dropped over a continuous belt of steel plates called the cane-carrier, moving over roller chains. From the cane-carrier, these are conveyed to a crusher fitted with a set of revolving knives and cut into very small pieces. These small pieces in the form of a compact blanket are made to pass through two roller crushers and four sets of mills. After major quantity of the juice has been extracted by the crushers and the first two mills, cold or hot water is sprinkled over the *bagasse* whereby residual juice gets diluted and can be easily extracted by further milling. About 90-95% of the juice is usually extracted. Though 98-99% of the juice can be extracted by repeated milling after sprinkling water on the *bagasse*, yet it is not desirable. Intensive milling results in the increase of colloidal matter in the juice and the cost of evaporation supersedes the gain in the form of juice. The juice extracted is weighed or measured as desired and sent for clarification.

In case sugar is to be extracted from sugar-beet, it is sliced and put in hot water when the sugar present in the beet diffuses out. A number of tanks are used and worked on the *principle of counter-currents*—concentrated solution comes in contact with fresh slices and the exhausted slices come in contact with fresh water and lose last traces of sugar in them. The solution obtained is treated like cane-juice.

(2) **Clarification of juice.** The raw juice is a dark opaque liquid containing about 15% sucrose and small quantities of glucose, fructose, vegetable proteins, mineral salts, organic acids, colouring matter, gums and fine particles of *bagasse* suspended in it. Allowed to remain untreated for some time, it begins to ferment and the sucrose present changes to mixture of glucose and fructose (*Invert sugar*). In order to avoid this, the juice is not allowed to stand untreated for a long time.

There are two main processes for clarification of juice :

(*i*) *Sulphitation.* Adding milk of lime and treating with sulphur dioxide.

(*ii*) *Carbonation.* Adding milk of lime and treating with carbon dioxide.

Both have advantages of their own. In fact combination of both is made use of to get better results.

(*a*) **Defecation.** The juice is strained to remove suspended matter and treated with 2-3% lime till the *p*H value reaches 7·2 in tanks heated with steam coils.

Heating of the juice helps the coagulation of albuminoids by lime. The vegetable proteins are thus coagulated and the organic acids neutralized. These form a scum on the surface of the juice when the hot juice is transferred to settling tanks called *subsiders*. The scum at the surface and the mud settling at the bottom are mechanically removed by passing the whole through a filter press, and the clear solution sent on to the conical tanks for carbonation or sulphitation.

(*b*) **Carbonation or Sulphitation**. A current of carbon dioxide is passed through the defecated juice, which contains unreacted lime and calcium sucrosate (*carbonation*). This removes the excess of lime as calcium carbonate and decomposes calcium sucrosate.

$$\underset{\text{Cal. sucrosate}}{C_{12}H_{22}O_{11}.3CaO} + 3CO_2 \rightarrow \underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + 3CaCO_3$$

Very often defecated juice is treated with sulphur dioxide (*sulphitation*) instead of carbon dioxide which serves the same purpose and bleaches the juice in addition, and produces a juice with much lighter colour. It prevents formation of brown mass by oxidation, and brings about coagulation of gums and albuminoids more effectively. During the process of sulphitation the solution is maintained neutral. In some cases '*sulphitation*' follows '*carbonation*'. The juice is filtered again to remove the precipitates.

At present all big sugar factories in India are following double carbonation and double sulphitation process for the manufacture of cane-sugar.

(3) **Concentration and Crystallization**. The clear juice is concentrated in a multiple effect evaporator (Fig. 49·1). Juice in the first pan is heated by exhaust steam from the engines of the factory. The concentrated juice from the first is taken to the second pan and heated there at a lower pressure, by steam from the first evaporator. The concentrated solution from the second pan is taken to the third pan and heated there at a still lower pressure by exhaust steam from the second evaporator.

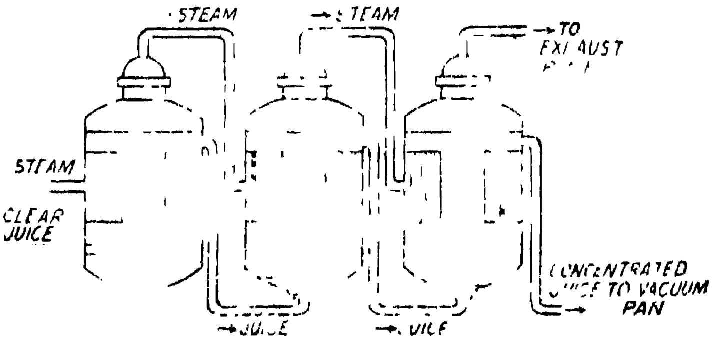


Fig. 49·1—A diagrammatic representation of the multiple effect evaporator

To this concentrated juice sulphur dioxide is again applied. All through this process a strict control is maintained over the acidity.

of the solution otherwise there will be losses due to inversion, destruction or even discoloration may be there.

The clear syrupy juice is just boiled in a vacuum pan till formation of sugar crystals begins. The contents of the vacuum pan (*massecuite*) are taken into the crystallizing tank and allowed to cool slowly when the tiny crystals of sugar grow in size.

(4) **Separation of Crystals.** The crystals along with the mother liquor (*Molasses*) are whirled in centrifugal machines wherein the molasses is removed. A little molasses adhering to the crystals is removed by spraying cold water on the crystals and whirling in the centrifuge again. The crystals are given a little blue colour and dried by dropping through a long pipe through which hot air is passing up and bagged

(5) **Refining of Sugar.** Sugar in India is generally put in the market as obtained in the above process. In foreign countries it is further refined by dissolving the crystals in hot water and decolorising the solution with animal charcoal or norit (coconut charcoal). This is followed by filtration, concentration under reduced pressure and crystallization as usual.

(6) **Recovery of Sugar from Molasses.** The molasses still contains sufficient amount of sugar. It is boiled over again to get a fresh crop of crystals. To recover sugar from the final molasses, the latter is treated chemically. It is diluted and treated with hot concentrated solution of strontium hydroxide. Sucrose present forms a precipitate of strontium sucrosate. This is separated, suspended in water and treated with carbon dioxide when strontium carbonate separates as white precipitate and sucrose present in the solution is decolorised, concentrated and crystallized as above.

$$\underset{\text{Strontium sucrosate}}{C_{12}H_{22}O_{11}.2SrO} + 2CO_2 \rightarrow \underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + 2SrCO_3$$

In India sugar is not extracted chemically from molasses although still about 30 to 35 per cent sugar is there. It is now being sent to distilleries where it is fermented and used in the manufacture of alcohol.

15. **Sugar Industry in India.**—India is the accredited birth-place of sugarcane and sugar. However, the industry progressed considerably after 1931 when it was granted protection. Number of sugar mills increased from 138 in 1950-51 to 315 in 1980-81. Today, the industry is the second largest in India, next only to textiles. The industry employs about 1·5 lakh workers, both skilled and unskilled. The industry is highly concentrated in U.P and Bihar though a trend towards dispersal is also noticeable.

Estimated production of Sugar in India (*in lakh tonnes*)

1960-61	1965-66	1970-71	1975-76	1979-80	1980-81
30·2	35·4	37·4	42·5	38·6	64·6

The industry is experiencing difficulty in promoting exports as well, because of the high cost of domestic sugar. This is due to several weaknesses of the industry, *viz.* (*i*) low yield per acre of cane in India which is just 15 tonnes as against 62 and 56 tonnes in Hawaii and Java, (*ii*) high price of cane which constitutes 60% of the cost of production of sugar and low sucrose content, (*iii*) uneconomic size of many sugar factories, and (*iv*) short crushing season which lasts only 145 days in a year in India.

There are three **by-products of sugar industry**, *viz.*, bagasse, molasses and press-mud. Bagasse was being used mainly as fuel for steam raising. In the Sixth Five-Year Plan it is going to be used for the manufacture of paper pulp, cardboard and insulation board. Molasses has demand in the preparation of acetic acid, aconitic acid, power alcohol, chemicals, chloroform, plastics, etc. Press-mud finds use in the manufacture of carbon paper and polish.

16. Properties of Sucrose : Physical. It is a colourless, crystalline substance (m.p. 461K), sweet in taste and very soluble in water, but only sparingly soluble in alcohol. It is optically active (*Dextro-rotatory*) having specific rotation $[\alpha]_D = +66{\cdot}5^\circ$ but does not exhibit mutarotation.

Chemical. (*i*) **Action of heat.** When heated with a little water, it melts and gives an amorphous glassy mass (*barley sugar*) on cooling.

On heating to about 470K, it loses water and gives *caramel* (brown mass) used in confectionery and colouring wine, etc. At still higher temperature it carbonises to give sugar charcoal.

(*ii*) **Hydrolysis.** On warming with dilute mineral acids, it gives glucose and fructose by hydrolysis.

$$\underset{\substack{\text{Cane-sugar}\\ [\alpha]_D=+66{\cdot}5^\circ\\ (\textit{Dextro}\text{-rotatory})}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underbrace{\underset{\substack{\text{Glucose}\\ [\alpha]_D=+52{\cdot}5^\circ\\ (\textit{Dextro-})}}{C_6H_{12}O_6} \quad + \quad \underset{\substack{\text{Fructose}\\ [\alpha]_D=-92^\circ\\ (\textit{Laevo})}}{C_6H_{12}O_6}}_{\text{The mixture is } \textit{laevo}\text{-rotatory}}$$

The change is called *inversion* as *dextro*-rotatory sucrose changes into *laevo*-rotatory mixture of glucose and fructose.

(*iii*) **Oxidation.** With concentrated nitric acid sucrose is oxidised to oxalic acid.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + 18[O] \longrightarrow \underset{\text{Oxalic acid}}{6(COOH)_2} + 5H_2O$$

(*iv*) **Dehydration.** With concentrated sulphuric acid it loses water to give sugar charcoal (*charring of sugar*). A smell of sulphur dioxide is also noticed due to reduction of the acid.

$$C_{12}H_{22}O_{11} + [H_2SO_4] \longrightarrow \underset{\substack{\text{Sugar}\\ \text{charcoal}}}{12C} + [11H_2O + H_2SO_4]$$

$$C + 2H_2SO_4 \longrightarrow 2SO_2 + CO_2 + 2H_2O$$

(*v*) **Fermentation.** An aqueous solution of sucrose with yeast gives alcohol by fermentation.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11} + H_2O} \xrightarrow{\textit{Invertase} \text{ in yeast}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\underset{\substack{\text{Glucose or}\\ \text{Fructose}}}{C_6H_{12}O_6} \xrightarrow{\textit{Zymase} \text{ in yeast}} \underset{\substack{\text{Ethyl}\\ \text{alcohol}}}{2C_2H_5OH} + 2CO_2$$

(*vi*) **Formation of sucrosates.** Sucrose solution reacts with lime or strontia to give calcium or strontium sucrosate.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + 3Ca(OH)_2 \longrightarrow \underset{\text{Calcium sucrosate}}{C_{12}H_{22}O_{11}.3CaO} + 3H_2O$$

(*vii*) **Acetylation.** With acetic anhydride sucrose gives an octa-acetyl derivative showing the presence of eight hydroxyl groups in the molecule.

(*viii*) **Action of concentrated hydrochloric acid.** Conc hydrochloric acid on boiling with cane-sugar produces laevulinic acid

$$\underset{\text{Cane-sugar}}{C_{12}H_{22}O_{11}} \xrightarrow{\text{Conc. HCl}} \underset{\text{Laevulinic acid}}{CH_3COCH_2CH_2COOH}$$

It does not contain any aldehyde or ketone group. It does not, therefore, give the characteristic properties of monosaccharides, *e.g.*, (*i*) it does not reduce ammoniacal $AgNO_3$ or Fehling's solution, (*ii*) it is stable towards alkalis, (*iii*) it does not give any osazone with phenylhydrazine, (*iv*) it does not exhibit mutarotation.

17. **Uses.**—(*i*) As an article of food and as sweetening agent in sweets and drinks ; (*ii*) in fruit preservation ; (*iii*) in the preparation of oxalic acid in the laboratory ; (*iv*) for the manufacture of octa-acetate.

18. **Tests.**—(*i*) Heat some sugar in a dry test tube, a characteristic smell is noticed.

(*ii*) Heat some sugar with concentrated sulphuric acid. Charring takes place and a mixture of carbon dioxide and sulphur dioxide is evolved.

(*iii*) Sucrose gives Molisch's test as described under glucose (*see* page 3·95).

(*iv*) Boil some sucrose solution with a few drops of dilute hydrochloric acid and add Fehling's solution. A red precipitate is obtained due to its reduction to cuprous oxide. No reduction occurs if it is not first boiled with dilute acid.

Sucrose gives the Salivanoff's test and the Furfural test as given by fructose. It does not give osazone and does not turn brown when heated with sodium hydroxide solution (*Distinction from glucose and fructose*).

19. **Constitution.**—(*i*) Molecular formula of sucrose as determined from its analytical data and molecular weight determination is $C_{12}H_{22}O_{11}$.

(*ii*) On hydrolysis sucrose gives a mixture of glucose and fructose, showing that in the molecule of sucrose, glucose and fructose molecules are linked through an oxygen atom.

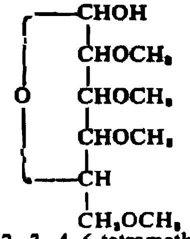
(*iii*) Sucrose is not a reducing sugar, *e.g.*, it does not reduce Fehling's solution and it does not give an oxime or an osazone. This, shows that neither the aldehyde group of glucose nor the ketonic group of fructose is free in sucrose.

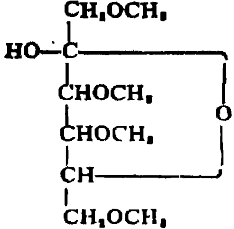
(*iv*) It gives octa-acetyl derivatives showing the presence of eight hydroxyl groups.

(*v*) On complete methylation sucrose yields the octamethyl derivative which, on hydrolysis, yields :

(*a*) 2 : 3 : 4 : 6-tetramethyl-δ-glucose, and

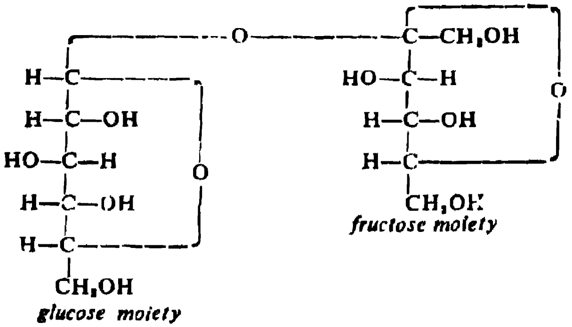
(*b*) 1 : 3 : 4 : 6-tetramethyl-γ-fructose,


2, 3, 4, 6-tetramethyl glucose (*Six-member δ-oxide ring*)


1, 3, 4, 6-tetramethyl fructose (*Five-member γ-oxide ring*)

This shows that carbon 5, in both cases, has no —OH group which could be methylated. Absence of —OH groups with these carbon atoms suggested that they must have participated in some ring formation in their respective hexose molecules.

Bearing in mind all the foregoing facts, the following structure was assigned to it by Haworth in 1927 :

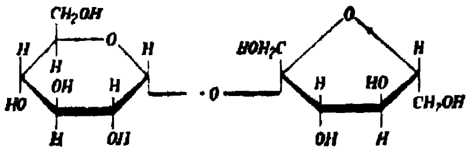


α-D-glucopyranosyl-β-D-fructofuranoside

or β-D-fructofuranosyl-α-D-glucopyranoside

(*vi*) Keeping all these facts in view, the structure shown above is assigned to sucrose and has been amply confirmed by further work.

The structure as well as the configuration of sucrose is represented by the following graphic formula :

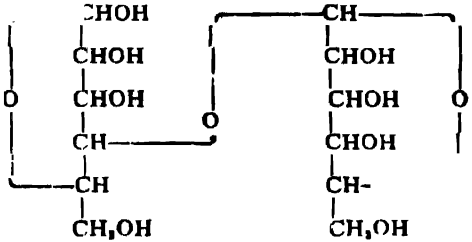

α-Glucopyranose β-Fructofuranose

It may be noted that the fructose molecule in sucrose exists as furanose ring (γ-form) and on hydrolysis the γ-form changes into the pyranose ring (δ-form).

20. Maltose, $C_{12}H_{22}O_{11}$.—It is obtained by the action of enzyme *diastase* present in malt on starch.

It is a white crystalline solid (m.p. 433-438K). It is very soluble in water and the solution is *dextro*-rotatory. It is sweet in taste and is about one-third as sweet as sucrose. It is a reducing sugar, *e.g.*, it reduces Fehling's solution. It forms an oxime and an osazone and undergoes mutarotation. This indicates that at least one aldehyde group of the two molecules of glucose is free in maltose. On hydrolysis with dilute hydrochloric acid or the enzyme *maltase* it gives glucose (2 molecules).

Its structure is shown to be as given below :

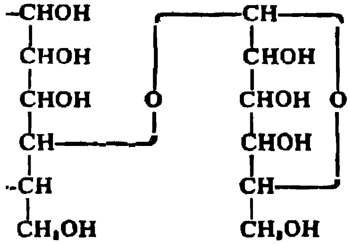


Maltose finds use in the manufacture of malted milk and various types of food for the infants.

21. Lactose (Milk Sugar), $C_{12}H_{22}O_{11}$.—It is present in the milk of all animals. It is manufactured from whey (a by-product obtained in the manufacture of cheese) by evaporation to crystallization.

It is a white crystalline solid (m.p. 476K with decomposition). It is soluble in water and the solution is *dextro*-rotatory and shows mutarotation. It is a reducing sugar and reduces Fehling's solution. It forms an oxime and an osazone. On hydrolysis it gives one molecule of glucose and one molecule of sugar called galactose.

Its structure has been shown to be :

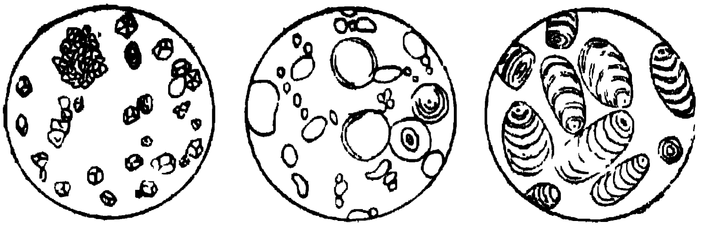


Lactose is sweet in taste but much less sweet as compared to sucrose. Relative sweetness of various sugars is as follows :

Sucrose	Lactose	Maltose	Glucose	Fructose
100	16	33	74·	173

POLYSACCHARIDES

22. Starch (Amylum), $(C_6H_{10}O_5)_n$.—Amylum is the ordinary starch which occurs in all green plants. A molecule of starch is built of a large number of α-glucose rings joined through oxygen atoms. Commercial sources of starch are wheat, barley, maize, potatoes and arrowroot. In these starch occurs in the form of loosely packed granules which vary in shape and size. Shapes of these granules as seen under a microscope are given below :



Potato Wheat Rice

Fig. 49·2—Starch granules as seen under microscope.

Manufacture. The process of manufacture of starch from corn or any of the other starchy materials consists in rupturing cell walls when the enclosed starch granules are exposed and washed to remove cellulose.

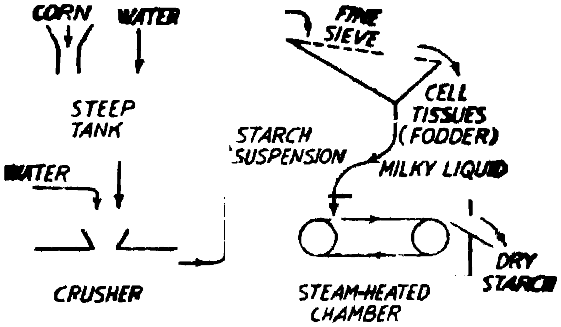


Fig. 49·3—Flow sheet for the manufacture of starch.

Cereal or plant, from which starch is to be manufactured, is washed with water in a washing machine when any dirt sticking is washed away. Rice, if used as raw material, is treated with dilute caustic soda solution before washing to remove gum and gluten (cellulose and protein materials). After washing, it is disintegrated mechanically when a paste-like mass called pulp is obtained containing starch granules exposed after disintegration along with finely divided fibrous tissue. The mixture is taken to a sifting machine and thoroughly washed with water and then sieved through fine brass-wire sieves when coarser particles of cellulose are left behind on the sieve and are used as fodder. Smaller particles of starch and some fibrous matter pass down as milky aqueous suspension. This is allowed to stand when heavier starch granules settle at the bottom. The lighter particles of cellulose are deposited to a very small extent and that too only in the last layers and are scraped off. The starch pulp so obtained is again treated with water when starch particles settle down and the supernatant layer is decanted off. It is then centrifuged to free it from the bulk of water present and slowly dried in air or by heating it gently in ovens till it contains only 12-20% moisture when it is ready for the market

Properties : Physical. Starch is tasteless, odourless, white amorphous powder insoluble in water. *Soluble starch* is obtained by heating ordinary starch with 10 per cent hydrochloric acid for 24 hours and then precipitating with alcohol. When boiled with water, starch granules swell up and burst to form a colloidal solution called starch paste. Starch granules vary in shape and size with the source.

Chemical. (*i*) *Action of heat.* When heated to 470-530K, starch changes into dextrin—a gummy substance used in calico-printing and as an adhesive. Charring occurs at higher temperature.

(*ii*) *Hydrolysis.* When boiled with dilute mineral acids, it is first converted into dextrin and finally into glucose.

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} \longrightarrow \underset{\text{Dextrin}}{(C_6H_{10}O_5)_{n_1}} \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6}$$

Both n and n_1 are unknown but n is believed to be greater than n_1.

Hydrolysis of starch with malt extract containing the enzyme diastase gives maltose.

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)_n} + nH_2O \xrightarrow[\text{malt extract}]{\text{Diastase in}} \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}}$$

(*iii*) *Action with Iodine.* With iodine starch gives a blue colour which disappears on heating to 350K and reappears on cooling (*A sensitive test for starch*).

Uses of Starch and its Derivatives. Starch and its derivatives are put to the following uses :

(*i*) It is one of the most valuable constituents of food as rice, bread, corn-flour, potato, etc.

(*ii*) In large quantities it is used for the manufacture of glucose.

(*iii*) It forms the basis of brewing industry as raw material in the manufacture of alcohol.

(*iv*) For the manufacture of dextrin and adhesives (starch paste).

(*v*) In paper industry it is used for sizing paper.

(*vi*) Its use in laundry as a stiffening agent and in toilet preparations is worth mentioning.

(*vii*) Used in textile industry for giving a finish to cotton fabrics.

(*viii*) Used in calico-printing as a thickening agent for colours.

(*ix*) Starch acetate, a derivative of starch, is a transparent gelatin-like mass. This is being used mainly for making sweets.

(*x*) Another derivative of starch is nitro-starch which is used as an explosive for blasting purposes.

Structure of Starch. It is now established that starch is a mixture of two components—α-amylose (17-34%) and β-amylose (amylopectin). In one of the several ways of separation, *n*-butyl alcohol is added to a hot colloidal solution of starch in water and the mixture is cooled. α-Amylose gets precipitated and is removed. Amylopectin is recovered from the mother liquor by adding methanol.

α-Amylose is soluble in water and gives a blue colour with iodine. Its molecular weight is of the order of 1×10^6. The molecule is a straight chain composed of approximately 300 glucose units.

Amylopectin is insoluble in water and gives a violet colour with iodine. Its molecular weight is of the order 5×10^4 to 10^6. It is commonly believed to be composed of three types of chains, each consisting of about 24 glucose units.

23. **Dextrin, $(C_6H_{10}O_5)_n$.**—It is prepared by the partial hydrolysis of starch with boiling water under pressure at 520K.

Dextrin is a white powder and finds use in sizing paper and in the manufacture of adhesives and confectionery.

24. **Inulin, $(C_6H_{10}O_5)_n.H_2O$.**—This special variety of starch occurs in dahlia tubers and Jerusalem artichokes. It is a white powder insoluble in cold water. With hot water it forms a colloidal solution which does not form a gel on cooling. It gives only fructose on hydrolysis and does not give any colour with iodine.

25. **Glycogen, $(C_6H_{10}O_5)_n$.**—It is called animal starch and is found in all animal cells, mainly in the liver. Its combustion supplies energy neede for life. It is a white powder soluble in water and the solution with dilute acid gives a purplish red colour with iodine. It gives glucose on hydrolysis.

26. **Cellulose, $(C_6H_{10}O_5)_n$.**—It is the main constituent of the cell walls of plants. Cotton and wood constitute two main sources of cellulose. Cotton and filter paper are almost pure cellulose.

Properties : Physical. Cellulose is a white amorphous solid, insoluble in water but soluble in ammoniacal copper hydroxide solution (*Schewitzer's reagent*).

Chemical. (*i*) *Action of Concentrated Sulphuric Acid.* Cellulose dissolves in cold concentrated sulphuric acid but is precipitated as amyloid on dilution.

Expt. Dip an ordinary paper in concentrated sulphuric acid for a moment and wash with water. The paper obtained with rough surface due to the precipitation of amyloid is called **parchment paper**.

(*ii*) *Hydrolysis.* On hydrolysis by boiling with dilute acid, cellulose gives glucose.

(*iii*) *Action of Alkali.* Cellulose is unaffected by dilute alkali. *If immersed in strong caustic soda solution, stretched cotton fibres swell and become rounded, stronger and more lustrous (silky appearance). This process is called* **mercerizing**.

(*iv*) *With Acetic anhydride,* cellulose forms triacetate.

(*v*) *Nitration.* With a mixture of concentrated sulphuric and nitric acids, it forms cellulose nitrate. *Gun cotton,* an explosive used in the manufacture of smokeless powders, is cellulose trinitrate.

Uses. It finds use in the manufacture of paper, rayon, celluloid, collodion films, cinema films and explosives, *e.g.*, gun cotton, cordite.

27. **Celluloid.**—The transparent plastic material obtained when poorly nitrated cellulose is heated with camphor under pressure is called *Celluloid*. It can be moulded while hot and is used in making toys and other articles of daily use.

28. Collodion.—It is 3·5 per cent solution of lower cellulose nitrate in alcohol (1 part) and ether (3 parts) and is being used in medicine, photography and in the manufacture of rayons.

29. Importance of Carbohydrates for the Living Systems.—Starch and sugars get hydrolysed to glucose by enzymes present in the various juices secreted by different organs in the human and animal digestive systems. Glucose so produced is transported from cell to cell by the blood. Slow combustion of glucose by a series of steps provides energy necessary for functioning of the living body and doing day's work. In plants glucose is carried from cell to cell by sap.

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O \; ; \; \Delta H = -2,832 \text{ kJ}$$

The body stores a part of carbohydrates for the rainy day in liver as glycogen called animal starch. In case of emergency like fasting or illness, glycogen hydrolyses to glucose and thus supplies the necessary energy.

No other food will act so quickly as sugar to supply energy when you feel exhausted. It is speedily digested, assimilated and converted into the requisite fuel.

Different enzymes are required for hydrolysis of cellulose. These are absent in the human body but present in the digestive system of various grazing animals which can, therefore, use cellulose of grass and plants as food.

30. Artificial Silk or Rayon.—The term rayon includes all synthetic fibres manufactured from cellulose. There are four processes for its manufacture :

(*i*) Cellulose nitrate process

(*ii*) Cellulose acetate process

(*iii*) Cuprammonium process

(*iv*) Viscose process.

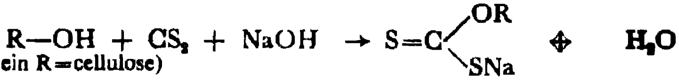
Today most of the rayon is manufactured by the viscose process and the term rayon is most often applied to viscose yarns. The cellulose needed for the manufacture of rayon is obtained from wood-pulp and cotton-linters. Yarn manufactured from other sources is inferior in quality.

(*a*) **Cellulose nitrate process.** Cellulose is nitrated with a diluted mixture of nitric and sulphuric acids when mono- and di-nitrates are obtained and are known as *pyroxylin* in the solid state. Pyroxylin is dissolved in a mixture of alcohol and ether to get collodion. This is forced through glass capillary tubes into the air when the solvent evaporates leaving behind threads of cellulose nitrate. These are digested with caustic soda or sodium bisulphite solution when the cellulose nitrate gives cellulose. The process is costly due to the high cost of chemicals required.

(*b*) **Cellulose acetate process.** Cellulose is treated with acetic anhydride in the presence of sulphuric acid when cellulose triacetate is obtained. This is decomposed with water to get the diacetate which is next washed, dried and dissolved in acetone mixed with some other organic solvents. The solution is forced through a spinneret into a warm chamber when the solvent evaporates leaving behind threads of cellulose acetate. The fibre obtained burns with difficulty but the process is costly. The product is termed *celanese silk.*

(*c*) **Cuprammonium process.** Cellulose is dissolved in ammoniacal copper hydroxide solution and the solution is forced through a spinneret into a sulphuric acid bath where the cellulose gets precipitated as fine threads. The fibre obtained is cheap and is known as *cupra silk*

(*d*) **Viscose process.** In the viscose process cellulose is soaked in a 20 per cent caustic soda solution for about three hours. The alkali solution is removed and the product is treated with carbon disulphide. This gives a mixture of cellulose xanthates which is dissolved in sodium hydroxide solution.



$$R{-}OH + CS_2 + NaOH \rightarrow S{=}C\begin{matrix} \diagup OR \\ \diagdown SNa \end{matrix} + H_2O$$

(Wherein R = cellulose)

Sod.cellulose xanthate

The alkaline solution of sodium cellulose xanthates has a high viscosity and is, therefore, called *viscose solution.* This is carefully filtered and forced through a spinneret into a bath of dilute sulphuric acid which hardens the gum-like threads into rayon fibres (Fig. 49·4).

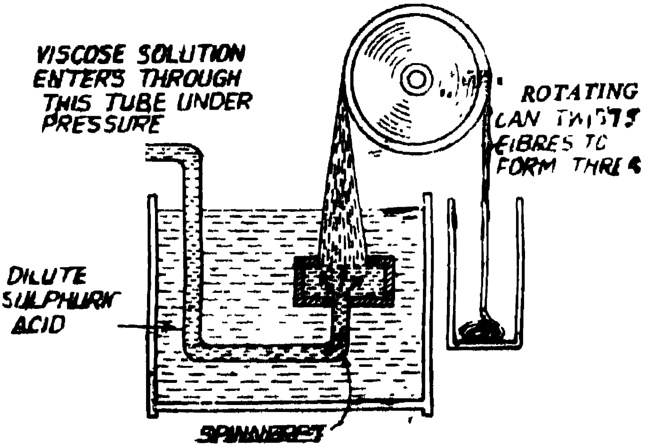

VISCOSE SOLUTION ENTERS THROUGH THIS TUBE UNDER PRESSURE
ROTATING CAN TWISTS FIBRES TO FORM THREAD
DILUTE SULPHURIC ACID
SPINNERET

Fig. 49·4—Spinneret used for making rayon.

The silk obtained by this process is termed viscose rayon. This is the cheapest process and commonly used.

30. Paper.—Paper is playing a very important role in our civilised society. It is at present an important means of transmission of thought through books, journals and newspapers. Chemically, paper is practically pure cellulose, $(C_6H_{10}O_5)_n$.

Raw materials used in the manufacture of paper. Formerly paper was manufactured almost exclusively from rags. At present it is prepared mainly from fibrous materials such as wood, straw, bagasse, bamboo, asparto grass and *bhabhar* grass. The choice of a particular raw material is determined by its economic as well as technical suitability. Various points considered are :

(*i*) Is there an ample supply of the raw materials ?

(*ii*) Is it available in all seasons of the year ?

(*iii*) The yield and quality of the fibre it gives.

(*iv*) Its cost of collection and transport as well as the cost of converting it into paper.

Manufacture of Pulp. The first step in the manufacture of paper is conversion of the fibrous material into pulp. Two processes used for the purpose are :

MECHANICAL PROCESS. Mechanical pulp is obtained from relatively soft wood like pine. The short, unbarked logs are subjected to mechanical grinding in presence of water. The pulpy material thus produced contains all the matter (ligno-cellulose) present in the original wood. Mechanical pulp is difficult to bleach and is used for manufacturing inferior paper such as newsprint, wall-paper, etc. This paper turns yellow with age and cannot, therefore, be used for printing books, etc.

CHEMICAL PROCESS. In this process the raw material is cut into chips and digested under pressure ("cooked") with *either* (*i*) a solution of calcium bisulphite, $Ca(HSO_3)_2$ (**Sulphite process**) *or* (*ii*) a solution of caustic soda (**soda process**). This dissolves out the *lignin* which together with cellulose makes up the solid part of its structure. The product obtained is more or less pure cellulose. It is technically known as "*half stuff*".

The pulpy material, so obtained, is washed and screened. It is then bleached by adding chlorine and water or with '*bleach liquor*'. The bleached pulp is beaten with water in a 'pulp beater'. Beating is the process of reducing the fibres to minute shreds and causing them to absorb and hold more water—an operation often referred to as '*hydration*'.

Filling and Sizing. The beater is used as a convenient place to mix 'filling materials, colouring matter and sizing materials. *Fillers* or *loading materials* are various inorganic substances like clay, calcium carbonate, calcium sulphate, talc, titanium dioxide and zinc sulphide. These give the proper body to paper, improve the appearance, make better printing surface, increase the opacity and reduce the cost.

Some ultramarine is added to give it the desired shade. Some other colouring materials may be added to give it the desired shade of colour.

To prevent spreading of ink as on a blotting paper, the paper requires "sizing". For this purpose some sizing materials like rosin, starch, glue or casein are either added to the beater or applied to the sheet of paper during its manufacture.

Manufacture of Paper. The thin suspension obtained from the beater is called *'soup'* by the paper maker. It is taken to a tank called the *'stock box'*. The soup is forced through a thin slit in the bottom of the stock box. It falls on an endless band of fine wire-gauze screen in motion. As the screen moves forward, the water present in soup drains through it and *the fibres mat together. The process of draining is assisted by vacuum from the suction boxes over which the wire-gauze screen travels.*

The fibrous sheet next passes between heavy press rolls covered with felt. Here the excess of water is removed. The sheet is then passed between drying cylinders which are steam heated. In some cases when sizing materials have not been added in the beater, these are applied here in the drier section or even after the driers. Sizing materials are made into a paste and applied to one or both sides of the paper sheet. The excess material is removed as the sheet passes between squeeze rolls.

Calendering. The surface of the dried sheet is generally rough and irregular. It is passed through a series of very hot and polished rolls. As a result of it the surface becomes compact and smooth and it takes a fine glaze. The process is known as *calendering.*

After calendering the sheet goes to the reel where it is wound into large rolls of finished paper. The roll when full is sent to the slitting machine for cutting paper into rolls of proper width and diameter.

Important uses of paper :

(*i*) Tissue paper is the lightest weight thin paper used for napkins, toilet papers and light weight wrappings.

(*ii*) For making bags and envelopes and as packing paper.

(*iii*) *For writing purposes.*

(*iv*) *For printing* books, journals and newspapers.

(*v*) *In buildings.* Thick bulky papers sometimes mixed with asbestos are employed in construction work. For example, *sheathing papers* to prevent wind from penetrating buildings ; felt papers for heat insulation ; felt papers saturated with asphalt to make roofing material ; deadening felt for acoustic properties in walls and floors.

(*vi*) In the manufacture of cardboard which finds a variety of uses such as making containers, wallboard, bottle caps and for binding.

Paper Industry in India. The manufacture of machine-made paper in India dates back to 1870 when the first mill was established on the Hooghly. There were 28 mills in 1952 with West Bengal accounting for 6 mills, Maharashtra 4 mills, Andhra and Karnataka 3 mills each, Orissa and Uttar Pradesh 2 mills each and Bihar, Gujarat, Haryana and Kerala 1 each. At present, *sabai grass* and *bamboo* are the principal raw materials for paper manufacture in India. There is only one newsprint factory at Nepanagar (Madhya Pradesh). Two other manufacturing units in the private sector have also been licensed with a total capacity of 90,000 tonnes. To meet the shortage of paper, it has been proposed to substitute bagasse (so far used as fuel in sugar industry) and other new raw materials for bamboo, raw material being used at present. There are proposals to manufacture paper from firewood.

The Hindustan Paper Corporation Ltd., New Delhi, set up in 1970 is a public sector undertaking. It has drawn up plans to set up three pulp and paper projects and one newsprint project. The Nagaland project with an annual capacity of 33,000 tonnes of writing and printing paper is expected to go on stream soon. The remaining two units—the Nowgong paper and pulp project and the Cachar pulp and paper project when set up will have an installed capacity of one lakh tonnes per annum each. The Kerala newsprint project started in 1975 at Velloor will have an installed capacity of 80 thousand tonnes per annum. It has started trial production.

Estimated Capacity and Production of Paper in India (*in th. tonnes*)

	1960-61	1965-66	1970-71	1975-76	1980-81
Paper and Paper board					
Capacity	410	770	1,000	1,058	1,058
Production	350	558	755	856	1149
Newsprint					
Capacity	30	30	30	75	75
Production	23	28	30	55	55

Although the paper industry has increased its production considerably, the output is not yet adequate. It is expected that Indian paper industry will soon meet the entire requirement of the country and may be in a position to export paper outside.

QUESTIONS

Essay Type :

1. What are carbohydrates and how are they classified ? Give examples. What is their importance in everyday life ? (*Mysore B Sc. 1976, 72*)

2. How is glucose manufactured ? Discuss briefly the properties of glucose (*Mysore B Sc. 1972*)

3. Discuss the structure of glucose giving the experimental evidence on which it is based. (*Kashmir B.Sc 1974 ; Delhi 1974 ; Agra 1973 ; Punjab 1976 Supp. ; Utkal 1975 , Karnatak 1972 ; Mysore 1976, 72*)

4. Discuss the configuration of glucose and furnish evidence in favour of its pyranose ring structure. (*Karnatak B.Sc. 1972 ; Mysore 1976*)

5. What is fructose ? How does it occur in nature ? How is the compound manufactured ? Describe its important reactions. (*Jabalpur B.Sc. 1976*)

6. How is fructose prepared ? Discuss the constitution and configuration of fructose. (*Punjab B.Sc. 1976 Supp.*)

7. Give an account of the important reactions in which glucose and fructose resemble aldehydes and ketones respectively. In what respects do they differ from them ?

8. How will you obtain : (*a*) Fructose from Glucose (or a ketohexose from an aldohexose) and *vice versa* ?

(*Kerala B.Sc. 1975 ; Nagpur 1974 ; Madras 1977 ; Delhi 1977*)

(*b*) Glucose from Arabinose (or an aldohexose from an aldopentose) and *vice versa*. (*Delhi B.Sc. 1977 ; Madras 1977 ; Utkal 1976*)

Or

Write an account of methods for

(*a*) Descending and ascending the sugar series.

(*b*) Conversion of an aldose into a ketose and *vice versa*.

(*Delhi B Sc. 1977, 71 ; Madras 1977*)

9. What is mutarotation ? How is it explained ?

(*Delhi B.Sc. Hons. Sub. 1979 Supp. ; Madras B.Sc. 1977, 75 ; Osmania 1979*)

10. (*a*) How is sucrose manufactured ? What do you know about sugar industry in India ? (*Delhi B.Sc. 1977 ; Nagpur 1976*)

(*b*) What are the chemical properties of cane-sugar.

(*c*) Discuss the evidence on which the structure of sucrose is based.

11. Compare the physical and chemical properties of glucose, fructose and sucrose. (*Karnatak B.Sc. 1972*)

12. Discuss the manufacture of starch. Give the industrial applications of starch and cellulose. (*Mysore B.Sc. 1973*)

13. Write notes on :

(*a*) Artificial silk. (*Agra B.Sc. 1973*)

(*b*) Manufacture of paper. (*c*) Celluloid.

(*d*) Soluble starch. (*Agra B.Sc. 1973*)

(*e*) Derivatives of cellulose. (*Madras B.Sc. 1977*)

14. Establish the open-chain formula of fructose. Write down its ring structure. How does the ring structure explain mutarotation exhibited by fructose ? (*Delhi B.Sc. 1977 Supp.*)

15. Give Amadori rearrangement for the formation of osazone from fructose. (*Delhi B.Sc. Hons. 1977*)

Short Answer Type :

1. What types of substances are included in the term carbohydrates now ?

2. Give molecular formulae of (*i*) Arabinose, (*ii*) glucose, (*iii*) fructose, (*iv*) sucrose, (*v*) maltose, (*vi*) starch, (*vii*) cellulose.

3. Write equations for the hydrolysis of (*i*) sucrose, (*ii*) starch, (*iii*) inulin.

4. Write equations for the action of (*i*) acetic anhydride, (*ii*) methanol, (*iii*) lime, (*iv*) Br_2 water, (*v*) HNO_3, (*vi*) Conc. HI+Red P at 370 K, (*vii*) HCN on glucose and fructose

5. What is the action of phenylhydrazine, hydroxylamine, caustic soda, conc. HCl and yeast on glucose and fructose ?

6. Write equations for the conversion of glucose into fructose and *vice versa.* (*Delhi B.Sc. Hons. 1979*)

7. Write down the configurational formulae for D-glucose and D-fructose and answer the following question :

Would they give the same or different osazone ? Explain with equations. (*Burdwan B.Sc. 1977*)

8. Write equations for (*i*) hydrolysis, (*ii*) oxidation, (*iii*) dehydration, (*iv*) fermentation and acetylation of sucrose.

9. Write equations for the reaction of lime on glucose, fructose and sucrose.

10. Name the monosaccharides which the following give on hydrolysis :

(*i*) sucrose, (*ii*) maltose, (*iii*) lactose, (*iv*) starch, (*v*) inulin.

11. What is mercerizing ?

12. Name the various steps involved in the manufacture of paper.

13. How is glucose obtained from cane-sugar ? (*Delhi B.Sc. Hons Sub. 1977*)

14. Starting from glucose how can you obtain : (*i*) Osazone, (*ii*) Sorbitol, (*iii*) Fructose, (*iv*) *n*-Hexane ? (*Delhi B. Sc. Hons Sub. 1977*)

15. Why can't we subsitutate starch by cellulose (grass) in our food whereas grazing animals can ?

16. (*a*) What is the necessary condition for different sugars to produce identical osazones ? Give the mechanism of glucosazone and fructosazone formation.

(*b*) How would you convert glucose into gluconic and glucuronic acids ? (*Delhi B.Sc. 1979*)

17. Ketones cannot be oxidised by mild oxidising agent, yet fructose is oxidised by Fehling's solution. Explain.

18. Which of the following will give a positive test with Fehling's solution ?

(*a*) Cane-sugar
(*b*) malt sugar
(*c*) invert sugar
(*d*) glucose
(*e*) fructose
(*f*) mannose
(*g*) inulin
(*h*) starch
(*i*) lactose

19. Specific rotation of α-D-Fructose is −21·0°, that of β-D-fructose is −130·0°. Specific rotation of their equilibrium mixture has been found to be −92·0°. Calculate the percentage composition of the equilibrium mixture.

6

Proteins

1. Introduction.—Among the most important and abundant substances which make up the living organisms are the compounds called proteins. These have a variety of functions in the body. Some of these are fibrous and are the main components of the hair, muscles and skin. A number of them are present in the body fluids and serve as carriers of inorganic and organic compounds. In addition, proteins help in communication (nerves), defence (antibodies), metabolic regulation (hormones) and oxygen transport (haemoglobin). We are familiar with enzymes which act as catalysts and control many biochemical reactions which make it possible for us to live. These are protein catalysts. It is an essential constituent of our food. Animals can live without fat and carbohydrates for a long time but not without proteins. They require proteins for growth (*i.e.*, for building new cells) and maintenance (*i.e.*, for replacement of proteins lost by wear and tear of tissues). The name *protein* was given by Mulder (1838) and was derived from the Greek word *protios* (meaning to *take the first place*).

Plants build up their proteins from carbon dioxide, water, mineral salts in the soil (nitrates and ammonium salts) and solar energy. Animals derive their proteins ultimately from plants. Animals eat plants and during the process of digestion the plant proteins are hydrolysed by enzymes producing amino acids which are absorbed by blood and reach the various tissues. The animal proteins are synthesised from these amino acids. The approximate protein content of some common foodstuffs is given in the following table.

Table 50 1—Protein content of some common Foodstuffs

Foodstuff	Protein%	Foodstuff	Protein%
Milk	5	White of the egg	12·5
Cheese	33	Egg yolk	16
Peas	21	Meat	24-26
Potatoes	2	Banana	1·5
Wheat	14	Maize	10

2. Composition of Proteins.—Composition of protein varies with source. An approximate composition may, however, be given as : carbon 50-53% ; hydrogen 6·7% ; oxygen 23·25% ; nitrogen 16-17% ; sulphur about 1%. Other elements may also be present, *e.g.*, phosphorus (in nucleoproteins), iodine (in thyroid protein) and iron (in haemoglobin).

The molecular weights of proteins cannot be determined with high precision but all values recorded for the individual proteins point to very large molecules. Values of molecular weights below 20,000 are rare. Approximate values of molecular weights of some common proteins are given below :

Table 50 2

Proteins	Approx mol. wt.
Zein (from corn), pepsin and insulin	35,000-40,000
Egg albumin	45,000
Haemoglobin	60,000-70,000
Urease (an enzyme)	4,80,000
Certain plant viruses	10-50 million

Molecular complexity of proteins will be best indicated by a specific example. Taking 32,000 as molecular weight of casein, its molecular formula should be $C_{1116}H_{1760}N_{360}O_{148}S_8P_6$

3. **Nature of Proteins.**—We have read about polysaccharides, starch and cellulose which are made up of a large number of glucose molecules linked with each other. Proteins like the polysaccharides are all polymeric substances. All proteins, when subjected to treatment with strong acids, depolymerize into their monomeric components, all of which are α-amino acids of the general formula given in the margin. The symbol R represents an organic radical which may range from an H atom to a large aliphatic or aromatic group as given in Table 50·3.

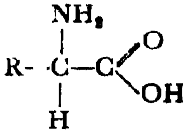
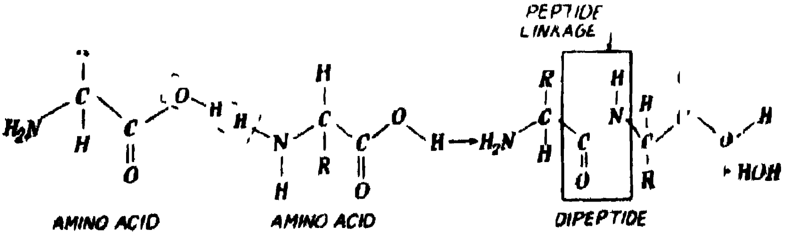


Table 50·3—Composition of R for a few amino acids

Name (Symbol)	R	Name (Symbol)	R
Glycine (*gly*)	H	Aspartic acid (*asp*)	HOOC.CH_2–
Alanine (*ala*)	CH_3—	Glutamic acid (*glu*)	HOOC.CH_2.CH_2–
Valine (*val*)	$(CH_3)_2CH$—	Lysine (*lys*)	H_2N CH_2.CH_2.CH_2.CH_2–
Cysteine (*cys*)	HS—CH_2—	Phenylalanine (*phe*)	C_6H_5.CH_2–

Twenty six different amino acids have been isolated from protein breakdown, of which eight are **essential amino acids** since they cannot be synthesised by man and must be included in the diet for proper health.

One of the most important chemical properties of amino acids is their ability to link together with the loss of a water molecule, forming a **peptide linkage** as a result of reaction of the acid group on one molecule with the basic group on another.



The dipeptide obtained contains a free —NH_2 group and a free —COOH group. Thus it is possible for more amino acids to couple to the dipeptide forming a tripeptide or a tetrapeptide or to continue until a large number of amino acids are linked together into a long chain. The resulting complex macro molecule is termed a polypeptide, a condensation polymer in which the amino acids are the repeating units.

A polypeptide with molecular mass greater than 10,000 amu is termed protein by convention.

Proteins may thus be defined as ***high molar mass compounds consisting largely, or entirely, of amino acid chains.***

Different polypeptides can differ from one another in an unlimited fashion. For example,

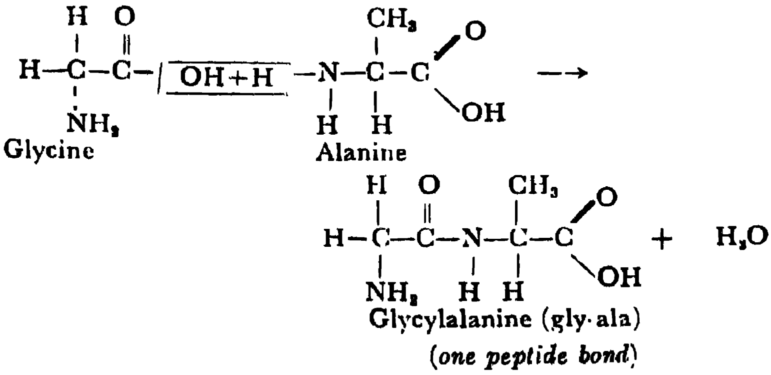
(*i*) Nature of amino acid or acids may be different.

(*ii*) Number of amino acids present may be different.

(*iii*) Even when nature and number of amino acids are the same, they may differ in the specific sequence in which these are joined. For instance three amino acids (say A, B, C) may be found arranged in 3 ! or 1×2×3=6 different ways indicated by ABC, ACB, BCA, BAC, CAB, CBA, in six different polypeptides. Thus unlimited number of proteins can be built from α-amino acids.

4. Primary, Secondary, Tertiary and Quaternary Structures of Proteins.—

(*a*) **Primary Structure of Proteins.** *The primary structure of a protein refers to the number and sequence of the amino acids in its polypeptide chain(s).* By convention, the structure of peptides is represented beginning with the amino acid whose amino group is free (popularly known as the N-terminal end). Free carboxyl group (the so-called C-terminal end) forms the other end of the peptide. While naming the peptide, each amino acid present (except the C-terminal amino acid) is named as an acyl group (wherein suffix *ine* is replaced by *yl*). For example, the dipeptide obtained from glycine and alanine is named as glycylalanine (gly-ala).



$$\mathrm{H-\underset{NH_2}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-\boxed{OH+H}-\underset{H}{N}-\underset{H}{\overset{CH_3}{C}}-C\overset{\nearrow O}{\underset{\searrow OH}{}}} \longrightarrow$$

Glycine Alanine

$$\mathrm{H-\underset{NH_2}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-\underset{H}{N}-\underset{H}{\overset{CH_3}{C}}-C\overset{\nearrow O}{\underset{\searrow OH}{}}} \quad + \quad H_2O$$

Glycylalanine (gly·ala)

(*one peptide bond*)

Similarly, tripeptide obtained from alanine, glycine and serine is named alanylglycylserine (ala-gly-ser, with two peptide bonds).

(*b*) **Secondary Structure of Proteins.** The primary structure tells us only about the sequence of amino acids in the protein chain. It tells us nothing about the shape or conformation of the molecule. Most of the bonds in protein molecules being single bonds, these can assume infinite number of shapes due to free rotation about single bonds. From a variety of physical measurements, it has, however, been found that each protein has only a single three-dimensional conformation. The fixed configuration of a polypeptide skeleton is referred to as the secondary structure of a protein. It tells us :

(*i*) about the manner in which the protein chain is folded and bent ;

(*ii*) about the nature of the bonds which stabilize this structure.

The Spiral Structure of Proteins. According to Linus Pauling and Robert Corey in some proteins polypeptide chains are coiled up like a spiral staircase to form a helix. This can be visualized as a spring coiled about an imaginary cylinder. The spring may be right or left-handed. It is, however, invariably found to be right-handed. The spiral being right handed is termed **α-helix.** In their helical structure NH group in one unit is linked to the carbonyl oxygen of the third unit by hydrogen bonding. This hydrogen bonding between different units is responsible for holding the helix in position. On an average there are about four amino acid units in each turn (gyre) of the helix

The side chains of these units project outward from the coiled backbone.

There are proteins like gamma globulin in which there is no helical structure. In protein like haemoglobin and myoglobin, certain regions of the polypeptide chain are helical while remaining portions possess random configuration. In proteins like silk fibroin and β-keratin the polypeptide chains are aligned side by side in a sheet-like arrangement. Hydrogen bonds between the adjacent chains stabilize them.

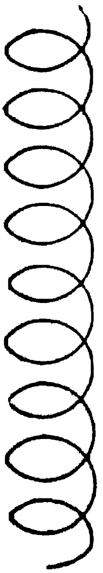


Fig. 50·1—Spiral structure of a protein

Wool fibre is very flexible and can be stretched to twice its normal length without breaking. It returns to its normal length when the tension is released. On stretching hydrogen bonds along turns of the α-helix break whereas the covalent bonds remain intact. On release of tension these hydrogen bonds are reformed and the helix is restored to its original size.

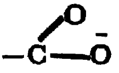
In silk fibre the polypeptide chains are aligned in sheet-like arrangement and held together very tightly by hydrogen bonding. Silk fibre is, therefore, very strong but resists stretching.

(*c*) **Tertiary structure of proteins.** We have so far pictured a protein as an α-helical structure drawing its strength from intrapolypeptide hydrogen bonding. In an aqueous solution water can successfully compete for these hydrogen bonding sites on the α-helical backbone. With the rupture of internal bonds, protein should assume a random configuration followed by disruption. Experimental evidence, however, has shown that protein retains its helical structure even in aqueous solution. From this we conclude that there are certain other forces involved which keep the long spiral chains tightly compressed into a definite geometrical structure characteristic of the protein.

This characteristic three-dimensional shape resulting from the precise folding and bending of the helical coil, is termed as the **tertiary structure** *of the protein.*

Various linkages responsible for the tertiary structure are given below. These depend on the nature of the amino acid side chains in the molecule.

(*a*) *Salt linkages* or ionic bonds between positively and negatively charged groups present on the side chains, *e.g.*, between



and $H_3\overset{+}{N}$—

(*b*) *Hydrogen bonding*

(*c*) *Disulphide linkage, e.g.*, in —CH_2—S—S—CH_2—

(*d*) *Hydrophobic interactions.* Non-covalent hydrophobic forces are important not because they are very strong but because there are so many of them.

(*d*) **Quaternary structure of proteins.** Some proteins have been found to be merely aggregates of polypeptide sub-units.

The manner in which various separate polypeptide chains fit together in these proteins containing more than one chain is termed as the quaternary structure of the protein.

5. Classification of Proteins according to Composition.—Based on the molecular structure and functions they perform, proteins are of the following two types :

(*a*) **Fibrous Proteins.** Their long and threadlike molecules lie side by side forming fibres. In some cases the molecules are held together by hydrogen bonds. On account of the strong intermolecular forces, these are insoluble in water. On account of their insolubility and fibre-forming tendency these are suitable as chief structural materials of animal tissues. Some examples of fibrous proteins are :

(*i*) *Keratin* in hair, nails, skin, wool, horns and feathers.

(*ii*) *Collagen* in tendons. (*iii*) *Myosin* in muscle.

(*iv*) *Fibroin* in silk.

(*b*) **Globular Proteins.** Molecules of globular proteins are folded forming compact units of nearly spheroidal shapes. Areas of contact between these units are small and hydrogen bonds are only internal. Inter-molecular forces in these are, therefore, comparatively weak and these are soluble in water or aqueous solutions of acids, bases and salts. Some examples of globular proteins are :

(*i*) All enzymes and many hormones, *e.g.*, insulin and thyroglobin.

(*ii*) Albumin in eggs.

(*iii*) Haemoglobin and fibrinogen in blood. Clotting of blood is due to conversion of fibrinogen into insoluble fibrous protein *fibrin*.

Various classes of proteins based on their physical properties, especially solubility, are :

(*a*) *Simple proteins* which give only amino acids on hydrolysis.

(*b*) *Conjugated proteins* which contain a non-protein part. The non-protein group is called *prosthetic group*.

(*c*) *Derived proteins*. These are degradation products obtained by hydrolysis of proteins with acids, alkalis or enzymes.

These are further subdivided as given in the tables below :

Table 50·4—Simple Proteins

Class	Characteristics	Examples with Sources
(*i*) Albumins	Soluble in water, acids and alkalis ; Coagulated by heat ; Precipitated on saturating with $(NH_4)_2SO_4$.	Serum albumin (*in blood*) Egg albumin (*in eggs*) Lactalbumin (*in milk*)
(*ii*) Globulins	Insoluble in water ; soluble in salt solution, acids and alkalis ; precipitated on half saturating with $(NH_4)_2SO_4$; coagulated by heat.	Serum globulin (*in blood serum*) Tissue globulin (*in tissues*) Vegetable globulin (*in seeds and nuts*)
(*iii*) Prolamines	Insoluble in water and salt solutions ; soluble in dil. acids or alkalis and in 70-93% alcohol.	Zein (*in maize*) Gliadin (*in wheat*) Hordein (*in barley*)
(*iv*) Glutelins	Insol. in water and salt soln. ; sol. in dil. acid and alkalis ; coagulated by heat.	Glutenin (*in wheat*) Oryzenin (*in rice*)
(*v*) Histones	Strongly basic ; sol. in water or dil. acid ; insol. in alkalis ; not coagulated by heat.	In haemoglobin and nucleoproteins.
(*vi*) Protamines	More basic ; sol. in water, dil. acids and ammonia ; not coagulated by heat ; precipitated from solution by alcohol.	In nucleoproteins
(*vii*) Scleroproteins (albuminoids)	Insol. in water or salt solution ; sol. in strong acids and alkalis ; not attacked by enzymes.	Keratin (*in hair or hoofs*) Fibroin (*in silk*)

Table 50·5—Conjugated Proteins

Class	Prosthetic group present and Characteristics	Examples with Sources
(*i*) Nucleoproteins	(Nucleic acid) They are weakly acidic ; soluble in water ; salt solution and alkalis.	In nucleus of cell.
(*ii*) Glycoproteins	(Carbohydrate or its derivative) They are acidic in nature and soluble in alkalis.	In egg white and jelly fish.
(*iii*) Phosphoproteins	(Phosphoric acid) They are insol. in water ; sol. in alkalis ; precipitated by acids from alkaline soln.	Casein (*in milk*) Viteline (*in egg yolk*)
(*iv*) Chromoproteins	(Pyrrole derivatives) Coloured bodies which usually contain metals like Fe, Cu, Mg, Co, etc.	Haemoglobin (*in blood*) Chlorophyll (*in plants*) In pigmented animal fibres. (*black wool and hair*)

Table 50·6—Derived Proteins

(*Produced when natural proteins are subjected to the action of enzymes and other hydrolytic agents*)

Class	Characteristics	Produced by
1. Denatured or coagulated proteins.	Insoluble in water.	Action of heat.
2. Primary proteoses. (*meta proteins*)	Insoluble in water or dil. salt solutions ; soluble in acids and alkalis.	Hydrolysis by alkalis or prolonged treatment with acids.
3. Secondary proteoses.	Soluble in water ; not coagulated by heat.	Graded hydrolysis with HCl or H_2SO_4.
4. Peptones.	Soluble in water ; not coagulated by heat ; give biuret test.	"
5. Peptides.	Soluble in water ; not coagulated by heat ; give no biuret test.	"

6. Classification of Proteins according to Functions.—Based upon functions, various classes of proteins are :

(1) **Structural Proteins,** like collagen found in skin, cartilage and bone.

(2) **Contractile Proteins,** *e.g.*, myosin and actin isolated from skeletal muscle.

(3) **Enzymes**. These are widely distributed protein catalysts vitally important to all living systems.

(4) **Hormones** Most hormones, *e.g.*, insulin are proteins.

(5) **Antibodies**. When foreign materials (antigens) are released into the body as a result of infection, the body itself produces certain antibodies to destroy the antigens. Gamma globulins are examples of antibodies

(6) **Blood proteins**. Three major protein constituents of blood are fibrinogen, albumins and globulins.

7. **Isolation of Proteins.**—Synthesis of proteins has not been found possible, they are always isolated from natural sources. Animal tissues or plant seeds are treated with a suitable solvent which dissolves the protein. Common solvents used for the purpose are water, 10% NaCl solution, 1% Na_2CO_3 solution, 0·1% NaOH solution, etc. From solution thus obtained, protein is precipitated with some suitable reagent, *e.g.*, alcohol, $(NH_4)_2SO_4$ or $MgSO_4$. In case more than one proteins are present, the individual proteins are separated by fractional precipitation using different concentrations of salt solutions.

8. **General and Physical Characteristics of Proteins.**—Proteins belonging to different classes possess different physical properties. Their physical characteristics in general can, however, be summarised as follows :

(*i*) Most of them are colourless (except chromoproteins), odourless and tasteless amorphous solids having no definite melting and boiling points. Some of them are crystalline in the pure form.

(*ii*) Barring a few exceptions (*e.g.*, insulin, egg albumin, etc.) proteins are hydrophilic colloids and cannot, therefore, diffuse through a semi-permeable membrane. Proteins are generally freed from salts by dialysis. Some of these (*e.g.*, gelatin and egg albumin) give thick sols with water and form gels on cooling.

(*iii*) Most of them are insoluble in water, alcohol and ether. But many of them dissolve in salt solutions, dilute acids and alkalis. A few of them (*e.g.*, those constituting skin, hair, etc.) are completely insoluble.

(*iv*) Their molecular weights are very high although these are not accurately known yet.

(*v*) They are optically active (laevo-rotatory), their activity arising from the fact that these are complex substances built up of amino acids.

(*vi*) *Coagulation.* Protein molecules are unstable structures which are readily altered by outside influences. On heating or on treatment with mineral acids the colloidal proteins are precipitated. The change is irreversible and is called *coagulation*.

Coagulation involves loss of many original physical properties, *e.g.*, solubility, physiological action, etc.) is referred to as *dena*[illegible] For example, egg albumin is coagulated or denatured on heating. Denaturing may also occur when protein remains in contact with water or alcohol for a long time or on adding heavy metal salts (*e.g.*, $CuSO_4$, $HgCl_2$, etc.).

(*vii*) *Salting out.* Proteins are precipitated from their colloidal solutions by saturating their solutions with readily soluble salts like $MgSO_4$ and $(NH_4)_2SO_4$. Precipitation also occurs on adding water soluble organic liquids like alcohol and acetone. The change is reversible and the precipitate obtained can be borught back intot he colloidal form by the addition of original solvent in excess. Such precipitation is termed salting out and must not be confused with coagulation which is an irreversible change.

9. Chemical Properties.—Proteins are built of α-amino acid molecules joined through peptide bonds as shown before. Thus proteins have free amino and carboxyl groups and give reactions of both like amino acids. Their important reactions are given below :

(1) **Formation of salts.** Due to the presence of basic $—NH_2$ group and acidic —COOH group, a protein gives salts with both acids and bases. Casein is present in milk as calcium salt.

(2) **Hydrolysis.** Proteins are hydrolysed when treated with acids, alkalis or enzymes. Hydrolysis occurs in steps and the ultimate products of hydrolysis are amino acids. Various steps involved are :

$$\begin{tikzcd} \text{Protein} \arrow[r] & \text{Primary proteoses (Cetaproteins)} \arrow[r] & \text{Secondary proteoses} \arrow[d] \\ \text{Amino acids} & \text{Peptides} \arrow[l] & \text{Peptones} \arrow[l] \end{tikzcd}$$

(3) **Oxidation.** Proteins get oxidised on burning or putrefaction. Various products of oxidation depending on conditions are nitrogen, amines, carbon dioxide and water. Foul smell from decaying dead body is due to amines produced as a result of bacterial oxidation of body proteins.

10. Tests of Proteins.—Proteins give a number of colour reactions. Specific colours obtained with certain reagents are used for identification of amines. Most of these colour tests depend upon reactions due to groups contained in one or more of the constituent amino acids. Thus a positive result in any one test may be given even by some non-protein substance. On the other hand, a true protein may not respond to a certain test if it happens to be deficient in that particular amino acid which gives that colour test. Thus, the presence or absence of protein can be shown conclusively only by using several of these tests. Various tests employed for detection of proteins are :

(*i*) *Biuret test.* Given substance is dissolved or suspended in strong caustic soda solution. A few drops of dilute copper sulphate solution are added to the above solution when a bluish violet, violet or pink colour is obtained if protein is present.

This test is due to the presence of —NH—CO— group as in biuret (*see* under Urea).

(*ii*) *Xanthoproteic test.* Given substance is warmed with nitric acid. A yellow colour, if produced, indicates the presence of a protein. Yellow stain on fingers while working with nitric acid is due to this reaction.

(*iii*) *Millon's test.* Millon's reagent is prepared by dissolving mercurous and mercuric nitrates in nitric acid. On adding this reagent to a solution of protein, a white precipitate is obtained which turns brick-red on boiling. This test is characteristic of —OH group present in the protein molecule.

(*iv*) *Molisch test.* An alcoholic solution of 1-naphthol is added to the protein solution taken in a test-tube. Concentrated sulphuric acid is then poured slowly along the sides of the test-tube. A violet colour is obtained at the junction of the two liquids. This test is given only by those proteins which contain a carbohydrate.

(*v*) *Hopkins Cole test.* Protein solution is mixed with a little glyoxalic acid and some concentrated sulphuric acid is poured along the side of the test tube when a bluish-violet colour is obtained.

(*vi*) *Lead sulphide test.* The given protein solution is boiled with caustic soda and lead acetate. A black precipitate is obtained. This test is characteristic of —S—S— or —SH groups.

(*vii*) *Ninhydrin test.* Proteins, having free —COOH and —NH_2 groups, give an intense blue colour with ninhydrin. This is an extremely delicate test.

(*viii*) *Coagulation test.* The protein solution is acidified with acetic acid and heated. Coagulation indicates the presence of albumin, a simple protein.

11. Uses of Proteins.

(*i*) *As Food.* The outstanding use of proteins is as food for man and beasts. Meat, eggs, fish and cheese production are some of the major industries based on the need for proteins in human food.

(*ii*) *In Textiles.* The textile fibres, wool and silk are both proteins. Artificial textile fibres have been manufactured from proteins, *e.g.*, *vicara* is produced from zein of corn.

(*iii*) *In controlling body process.* Haemoglobin present in blood is responsible for carrying oxygen and carbon dioxide. Hormones are secreted by certain glands and control various body processes. Haemoglobin and hormones are proteins.

(*iv*) *As enzymes.* Enzymes which are responsible for various fermentations are all proteins.

(*v*) *As anti-virus vaccines.* Viruses which cause diseases like rabies, smallpox, influenza, etc., are proteins. Thus proteins if denatured and introduced in the body give immunity from the disease to be caused by the original virus.

(*vi*) *In industry.* Leather is manufactured by tanning the proteins of animal hides. Gelatin is used in food products, photographic films. Glue is used as an adhesive and in sizing paper. Casein is manufactured from milk and used in the manufacture of leather, paper, textiles, cold-water paints and adhesives.

(*vii*) *In the manufacture of Amino acids.* Amino acids needed for medicinal use and feeding experiments are prepared by hydrolysis of proteins.

12. Estimation of free Amino and Carboxyl groups.—Amino acids are present in aqueous solution mainly as zwitter ions which have a buffering effect. Amino acids cannot, therefore, be titrated with a standard alkali directly. Special methods given below are used for the estimation of amino and carboxyl groups by suppressing the formation of zwitterion.

(*a*) **Estimation of Amino group.** Amino group in amino acid can be estimated by its titration in glacial acetic acid (as solvent) against acetous perchloric acid) ($HClO_4$ in glacial acetic acid). The presence of glacial acetic acid (solvent) enhances the basic properties of the free amino group, and its titration with acetous perchloric acid becomes possible.

$$H_2NCHR{-}COOH \rightleftharpoons H_3\overset{+}{N}CHRCO\overset{-}{O}$$

$$H_2NCHRCOOH + HClO_4 \longrightarrow [H_3NCHRCOOH]^+ + ClO_4^-$$

Weigh out accurately about 3 milli-equivalents of the amino acid in a 250 cm^3 conical flask and add 50 cm^3 of 0·1 N acetous perchloric acid. Shake it vigorously till the amino acid is dissolved. Excess of the acid left unused is back titrated with 0·1 N-sodium acetate in acetic acid in the presence of 2-5 drops of crystal violet or methyl violet (*indicator*). First appearance of a violet tinge is the end point

$$HClO_4 + CH_3COONa \xrightarrow{CH_3COOH} NaClO_4 + CH_3COOH$$

Perform a blank experiment by treating 50·0 cm^3 of the 0·1N perchloric acid with sodium acetate solution.

Calculate the percentage of amino group (Eq wt = 14) in the given amino acid from the formula :

$$\%\ \text{Amino group} = \frac{(V_1 - V_2) \times N_1 \times 14 \times 100}{W \times 1000}$$

where V_1 = volume (cm^3) of the sodium acetate solution used for blank ;

V_2 = volume (cm^3) of the sodium acetate solution used for sample ;

N_1 = Normality of sodium acetate solution.

W_1 = weight (*g*) of the sample;

(*b*) **Estimation of Carboxyl group by Formal titration.** An aqueous solution of the amino acid is treated with an excess of carefully neutralised solution of formaldehyde when the amino group condenses with formaldehyde forming a stable anion. The carboxyl group can then be treated with a strong alkali solution. Reaction probably proceeds in two steps given below :

(*i*) Neutralisation of the zwitterion by base.

$$\underset{\textbf{base}}{O\overset{-}{H}} + \underset{\textbf{zwitterion}}{H_3\overset{+}{N}CHRCO\overset{-}{O}} \rightleftharpoons \underset{\textbf{anion}}{H_2NCHRCO\overset{-}{O}} + H_2O$$

(*ii*) Neutralization is followed by or accompanied by condensation of anion with formaldehyde.

$$HCH=\boxed{O + H_2}NCHRCOO \rightarrow \underset{\text{stable anion}}{CH_2=NCHRCOO} + H_2O$$

Condensation results in blocking the amino group and leaves the — COOH group free to react with a strong base

About 30 milli-equivalents of the given amino acid are accurately weighed and taken into a 250 cm³ measuring flask. It is dissolved in boiled-out distilled water and volume made up to the mark. It is shaken vigorously to make a homogeneous solution.

Neutralise 50 ml of formalin in a conical flask by titrating with 0·1N-NaOH in the presence of thymolphthalein indicator till the solution has a greenish colour.

Take 25 cm³ of the amino acid solution prepared above in a conical flask and add 10 cm³ of the neutral formaldehyde. Titrate it with 0·1N -$Ba(OH)_2$ solution till the colour changes blue.

Calculate the percentage of the carboxyl group (—COOH, Eq wt=45) in the amino acid from the following formula :

$$\% \text{ of } —COOH = \frac{V_1 \times N_1 \times 45 \times 100}{W \times 1000}$$

where V=vol of $Ba(OH)_2$ solution (cm³)

N= normality of $Ba(OH)_2$ solution

W=Wt (g) of amino acid sample taken.

QUESTIONS

Essay Type :

1. What are proteins ? How are they classified ? Distinguish between fibrous and globular proteins as to structure and physical characteristics. (*Andhra B.Sc. 1974*)

2. (*a*) What do you know about the composition and structure of proteins ? What is the order of their molecular weights ?

(*b*) Give the colour reactions of proteins. (*Mysore B.Sc. 1972*)

3. Write an account of the general properties and uses of proteins.

4. What specific tests are employed for detecting proteins ?

5. Give an account of the classification of proteins and describe the important methods for the synthesis of α-amino acids.

6. Give an account of the structure and configuration of proteins.

7. What are the prosthetic groups ? How are proteins classified on the basis of prosthetic groups ? (*Delhi B.Sc. Hons. 1976*)

8. Give the α-helix structure of a protein molecule. What are the binding forces which help in the formation of coils of proteins ? (*Delhi B.Sc. Hons. 1978*)

9. The folded and coiled amino-acid chain in proteins is stabler than an open and linear chain. Explain why. (*Delhi B.Sc. Hons. 1977*)

Short Answer Type :

1. What are proteins ?

2. What are various functions of proteins ?

3. Arrange the following in the decreasing order of their protein content : Potatoes, cheese ,banana, meat, egg yolk.

4. What are essential amino acids ?

5. What is peptide linkage ? What are dipeptides and tripeptides ?

6. What are proteins used a catalysts called ?

7. What are products of hydrolysis of proteins ?

8. What are products obtained on oxidation of proteins ?

9. Name two textile fibres which are proteins.

10. Discuss the use of proteins in controlling body processes.

11. What is the difference between a polypeptide and a protein ?

12. What are conjugated proteins ? How are they classified ?
(Delhi B.Sc. Hons. 1976)

13. How may different polypeptides differ from one another ? What do you know about the spiral structure of proteins ?

14. Write a note on uses of proteins ?

15. What are the building blocks of proteins ? What are fibrous proteins ? Give two-characteristics of these.

16. What are globular proteins ? Give two characteristics of these.

17. What is denaturation of protein ?

18. What are the functions of proteins in the body ?

19. Give the names of four conjugated proteins and indicate the nature of their prosthetic groups. To what general class of conjugated proteins does each belong ?

20. Let the letters A, B, C, and D represent four different amino acids. Construct all the possible tetrapeptides using each letter only once.

21. Write the formula if a β-amino acid and write its IUPAC name.

22. What is meant by the primary, secondary, tertiary and quaternary structures of proteins ?

23. Briefly describe on the molecular level what occurs during each of the following :

(*a*) boiling an egg (*b*) sterilization of surgical instruments.

(*c*) Use of dilute silver nitrate solution as disinfectant in the eyes of newborn infants.

24. Glycine and alanine on condensation yield a mixture of four dipep-
Explain. *(Delhi B.Sc. Hons. 1978)*

25. How do you estimate free amino and carboxyl groups in an amino acid ?

7

The Ureides

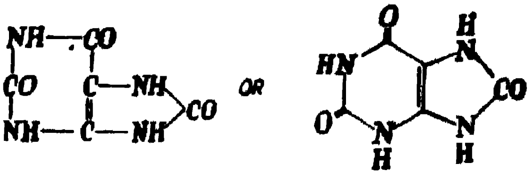
1. What are Ureides ?—Acyl derivatives of urea are called ureides and may be called *Acylureas.* For example, urea reacts with acetyl chloride or acetic anhydride to give acetyl derivative of urea (acetylurea)—the ureide of acetic acid.

$$NH_2.CO.NH_2+CH_3COCl \rightarrow \underset{\text{Acetylurea}}{CH_3CO.NHCONH_2}+HCl$$

These are compounds formed by condensation of urea with acids and contain the amide type (CO-NH) of linking.

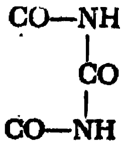
2. Classification.—Ureides have been classified in two different ways :

(*a*) *According to the number of urea residues present.* Those containing one urea residue are termed monoureides and others containing two urea residues are termed diureides. For example, acetylurea is a monoureide while uric acid is a diureide.

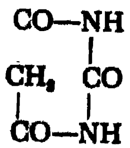


uric acid

(*b*) *According to Structure.* Based on the structure, the ureide is classified as (*i*) *acyclic or open chain ureide* if it has an open chain structure and as (*ii*) *cyclic ureide* if its molecule has a closed chain structure. For example, acetylurea given above is an acyclic or open chain ureide. Oxalylurea or parabanic acid and malonylurea or barbituric acid are two examples of cyclic ureides



oxalylurea or parabanic acid



malonylurea or barbituric acid

3. Preparation of Ureides.—General methods for preparation of ureides are :

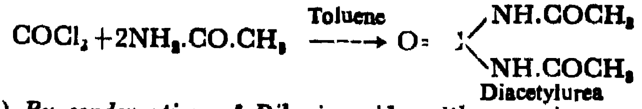
(i) *Mono-ureides are obtained by the action of an acid chloride, an acid anhydride or an ester on urea in an inert medium or pyridine.*

$$CH_3COCl + H_2N.CO.NH_2 \rightarrow CH_3CONH.CONH_2 + HCl$$

Acetylurea

Only one acyl group can be introduced into the urea molecule by this method.

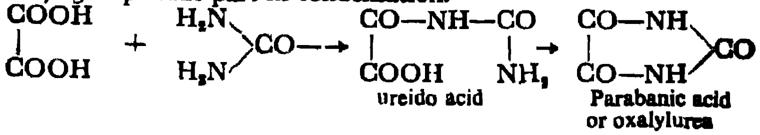
(ii) *Diacylureas can be prepared by the action of $COCl_2$ on acid amides :*



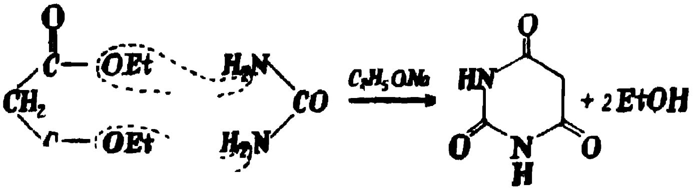
$$COCl_2 + 2NH_2.CO.CH_3 \xrightarrow{\text{Toluene}} O{=}C\begin{matrix} \diagup NH.COCH_3 \\ \diagdown NH.COCH_3 \end{matrix}$$

Diacetylurea

(iii) *By condensation of Dibasic acids with urea in presence of $POCl_3$ at 390 to 410K.* Two kinds of derivatives are obtained. When only one COOH group is involved in the condensation, *ureido acids* are formed whereas cyclic *ureides* are obtained when both the carboxyl groups take part in condensation.

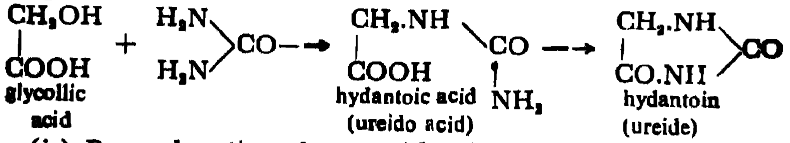


Cyclic ureides can also be obtained by refluxing a diester with urea in alcoholic solution in the presence of sodium ethoxide. For example, malonic ester gives malonylurea (*barbituric acid*).

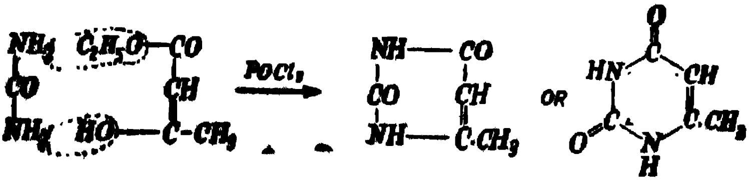


Barbituric acid
2,4,6-Trihydroxypyrimidine
(*Crystalline solid—m.p. 518K*)

Condensation with hydroxy acids containing one OH and one COOH group is similar.



(iv) *By condensation of urea with β-ketonic acids (or esters) and β-aldehydic acids.* Cyclic ureides so obtained are called *uracils.*



4. General Chemical Behaviour of Ureides—Ureides being acyl derivatives of urea, these contain two types of linking :

(*a*) —CO—NH—CO, the imide linking, and

(*b*) the NH—CO—NH—linking.

(1) Characteristic properties of the —CO—NH—CO—(imide) linkings are :

(*i*) The H atom of the NH is reactive and may be replaced by metallic atoms and subsequently by alkyl groups. Ureides are, therefore, soluble in alkalis.

(*ii*) On treatment with PCl_5 or PCl_3, it yields the corresponding chloro derivative, $-N{=}\overset{/}{C}-Cl$

(2) Ureides on hydrolysis yield urea and the parent organic acid (a characteristic property of the NH—CO—NH grouping).

(3) Malonylurea contains the linking $-CO-CH_2-CO-$ containing a reactive methylene group. The H atoms of the CH_2 group can be replaced by R, Br, NO and NO_2 groups.

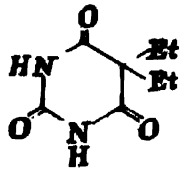
As five and six member rings are stable, cyclic ureides, so far known, are almost limited to those derived from oxalic acid and malonic acid and their derivatives.

Ureides of monocarboxylic acid like acetic acid are *simple ureides*. These are useful drugs particularly when the acid radical has a banched chain, *e.g.*, bromural.

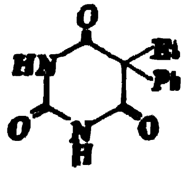
$$(CH_3)_2CH.CHBr.CO.NH.CONH_2$$

bromural (α-bromo-*iso*valerylurea)

Many of the cyclic ureides are excellent drugs. For example, barbituric acid and its derivatives given below are used in medicine as hypnotics and sedatives.



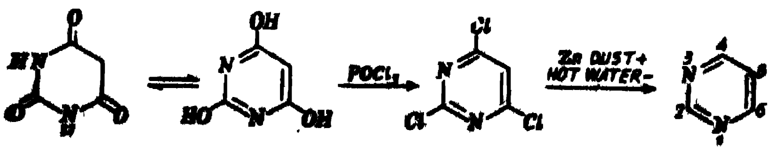
5 : 5-diethylbarbituric acid, barbitone or veronal (m.p. 464K)



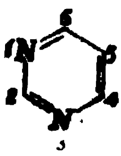
5-phenyl-5-ethylbarbituric acid, phenobarbitone or luminal.

Veronal is prepared like barbituric acid by condensation of diethylmalonic ester with urea in alcoholic solution in the presence of sodium ethoxide.

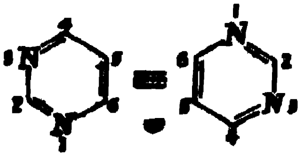
5. Pyrimidine.—Cyclic ureides containing six-member ring behave, in a number of ways, as pyrimidine derivatives. Pyrimidine was first prepared from barbituric acid (malonylurea) as follows :



Different atoms of the pyrimidine ring were formerly numbered as given in formula A below. According to the IUPAC system, these are now-a-days being numbered as shown in the formula B.

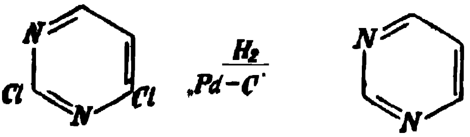


A

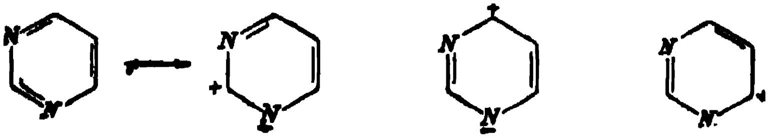


B

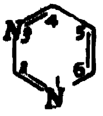
It can also be prepared by oxidation of alkylpyrimidines followed by decarboxylation. A recent method for the preparation of pyrimidine is the catalytic reductive dechlorination of 2, 6-dichloropyrimidine by heating with hydrogen under pressure in the presence of Pd—C and MgO.



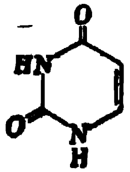
Pyrimidine is probably a resonance hybrid of the following resonating structures :



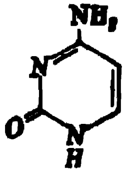
Relationship between pyrimidine and ureides will be seen from the formulae of uracil (2, 4-dihydroxypyrimidine) and cytosine (4-aminouracil or 4-amino-2-hydroxypyrimidine).



Pyrimidine

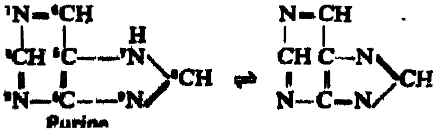


Uracil.



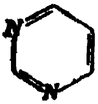
Cytosine

6. **The Purines.**—Compounds derived from two molecules of urea and one molecule of dibasic acid are called cyclic diureides. Purine is the parent substance of a group of cyclic diureides. It exists in two tautomeric forms given below :

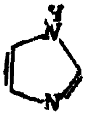


Purine

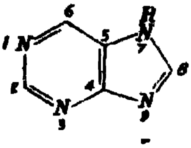
Its structure consists of a pyrimidine ring and an imidazole ring fused together.



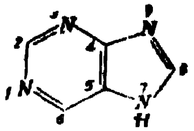
Pyrimidine ring



Imidazole or Iminazole ring

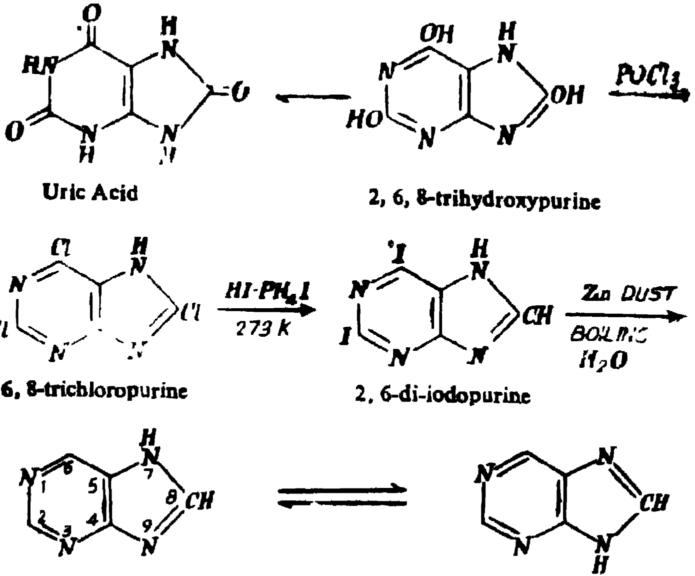


A



B (Modern)

Purine may be prepared from uric acid as follows :



Uric Acid

2, 6, 8-trihydroxypurine

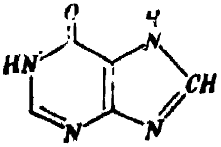
2, 6, 8-trichloropurine

2, 6-di-iodopurine

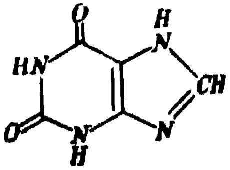
Purine (*Tautomeric formula*)

It is a colourless solid (m.p. 289-290K) highly soluble in water. It has both acidic and basic properties. Some important purine derivatives are uric acid, hypoxanthine, xanthine and caffeine.

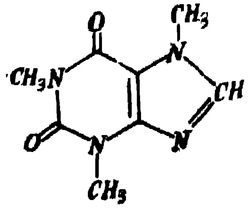
Uric acid as given above behaves as trienol (2, 6, 8-trihydroxypurine) when treated with POCl$_3$. Hypoxanthine is 6-hydroxypurine, xanthine is 2, 6-dihydroxypurine whereas caffeine is 1, 3, 7-trimethylxanthine.



Hypoxanthine



Xanthine



Caffeine

7. Uric acid, 2, 6, 8-Trihydroxypurine, $C_5H_4O_3N_4$.—It occurs in the urine of carnivorous animals. Human urine contains nearly 0·5% of acid ammonium urate. Normally only traces of it are present in the blood but in gouty persons the amount is considerably large. The excess of uric acid deposits in the joints causing gout or in the tissues causing rheumatism. Accumulation of the acid in the bladder of the kidneys results in the formation of stones. Excreta of birds and reptiles are rich in uric acid. Guano (excreta of certain sea birds or snakes) is a rich source of uric acid.

Preparation. (1) *From Guano.* Guano is powdered and boiled with caustic soda solution till no more ammonia is liberated. The hot solution contains sodium urate. It is filtered and poured in hydrochloric acid and allowed to stand when uric acid crystals separate. These are filtered and dried in air.

(2) *From Urine.* Urine is concentrated and treated with hydrochloric acid. Crystals of uric acid separate on standing.

Properties. It is white crystalline powder having no taste or smell. It is very sparingly soluble in water and insoluble in alcohol or ether. It decomposes when heated above 670K forming ammonia, urea, cyanuric acid, etc.

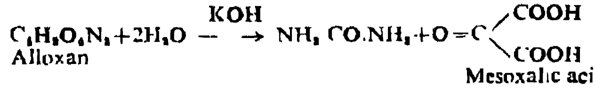
Uric acid behaves as a weak dibasic acid due to enolisation. With sodium carbonate, it gives an acid salt while with sodium hydroxide, a normal salt is produced. The acid salts are sparingly soluble in water while normal salts are moderately soluble in water. Lithium salts are freely soluble and this is the reason why lithia water is used as a remedy for gout.

Constitution. (1) Molecular formula of uric acid as deduced from its analytical data and molecular weight determination is $C_5H_4N_4O_3$.

(2) **Presence of Alloxan and Urea units in Uric acid.** On oxidation with nitric acid uric acid gives alloxan and urea.

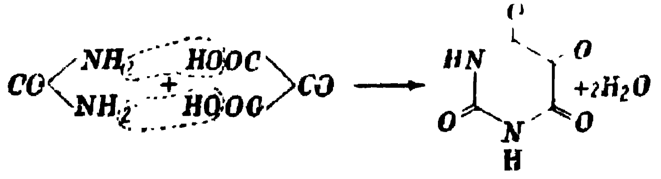
$$\underset{\text{Uric acid}}{C_5H_4N_4O_3} + H_2O + O \xrightarrow{HNO_3} \underset{\text{Alloxan}}{C_4H_2O_4N_2} + \underset{\text{Urea}}{H_2N\,CO.NH_2}$$

Structure of Alloxan. When hydrolysed with alkali, alloxan gives one molecule of urea and one molecule of mesoxalic acid.



$$\underset{\text{Alloxan}}{C_4H_2O_4N_2} + 2H_2O \xrightarrow{KOH} NH_2\,CO.NH_2 + \underset{\text{Mesoxalic acid}}{O{=}C\begin{cases}COOH\\COOH\end{cases}}$$

Since alloxan contains no free amino or carboxyl groups, the products of hydrolysis suggest it to be mesoxalylurea. This cyclic structure is confirmed by its preparation by direct union of urea and mesoxalic acid.



(3) Presence of Allantoin unit in Uric acid. When uric acid is oxidised with aqueous suspension of lead dioxide or with alkaline permanganate, the products are allantoin and carbon dioxide.

$$C_5H_4O_3N_4+H_2O+[O] \longrightarrow \underset{\text{Allantoin}}{C_4H_6O_3N_4}+CO_2$$

Structure of Allantoin

(*i*) Allantoin on hydrolysis with alkali gives two molecules of urea and one molecule of glyoxylic acid.

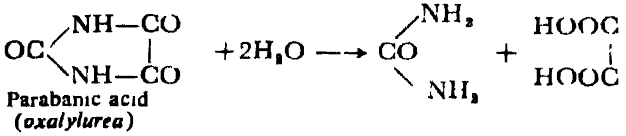
$$\underset{\text{allantoin}}{C_4H_6O_3N_4}+2H_2O \longrightarrow \underset{\text{urea}}{2NH_2.CO.NH_2}+\underset{\text{glyoxylic acid}}{CHO.COOH}$$

This suggests that the allantoin is the diureide of glyoxylic acid.

(*ii*) Allantoin yields urea and parabanic acid in equimolecular proportions when oxidised with nitric acid.

$$\underset{\text{Allantoin}}{C_4H_6O_3N_4}+[O] \xrightarrow{HNO_3} \underset{\text{Urea}}{NH_2.CO.NH_2}+\underset{\text{Parabanic acid}}{C_3H_2O_3N_2}$$

Parabanic acid on hydrolysis gives urea and oxalic acid which suggests it to be oxalylurea.

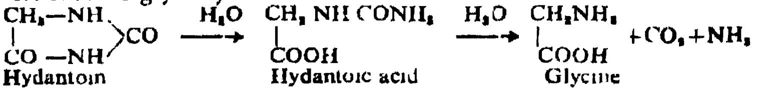


(*iii*) From this we infer that allantoin contains the parabanic acid nucleus joined to a molecule of urea. The point of attachment is deduced from the following experimental evidence :

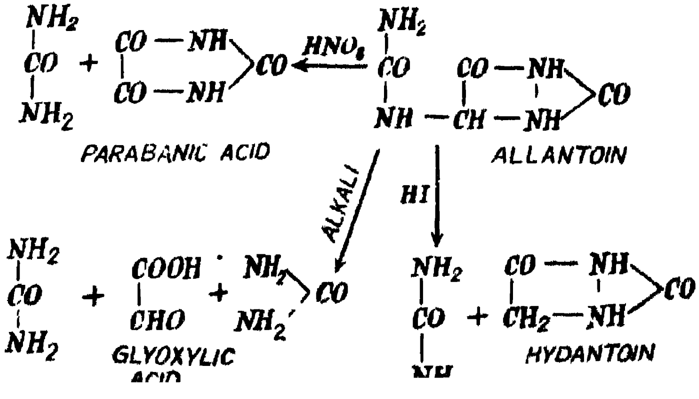
(*a*) Allantoin on reduction with conc. HI at 370K forms urea and hydantoin.

$$\underset{\text{Allantoin}}{C_4H_6O_3N_4}+2[H] \xrightarrow{HI} NH_2.CO.NH_2+\underset{\text{Hydantoin}}{C_3H_4O_2N_2}$$

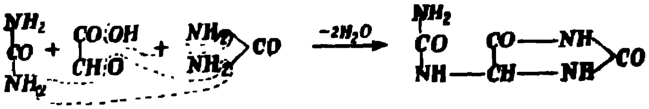
(*b*) Controlled hydrolysis of hydantoin yields hydantoic acid (ureido acetic acid) which on further hydrolysis gives glycine, ammonia and carbon dioxide. These products of hydrolysis suggest hydantoin to be glycollylurea.



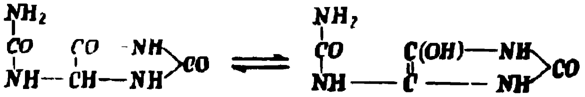
(*iv*) The following structure for allantoin would account for all of the foregoing results :



(*v*) This is confirmed by its synthesis by heating urea with glyoxylic acid at 370K.

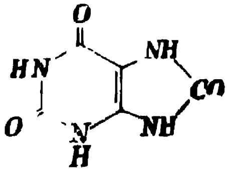


(*vi*) Allantoin contains a chiral carbon atom. Hence two optically active forms of allantoin should exist. These have actually been obtained. The two forms racemise rapidly in solution and racemisation occurs probably via enolisation.

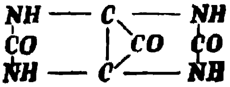


(4) **Structure of Uric acid deduced from Structures of Allantoin and Alloxan.** In the formation of allantoin from uric acid by oxidation, the latter loses one carbon atom as CO_2. The problem is, therefore, to fit in one carbon atom into the allantoin structure bearing in mind that the assigned structure includes the alloxan skeleton also—to account for the formation of alloxan on oxidation.

Two structures were proposed for uric acid, one by Medicus in 1875 and the other by Fittig in 1878.



Medicus formula



Fittig's formula

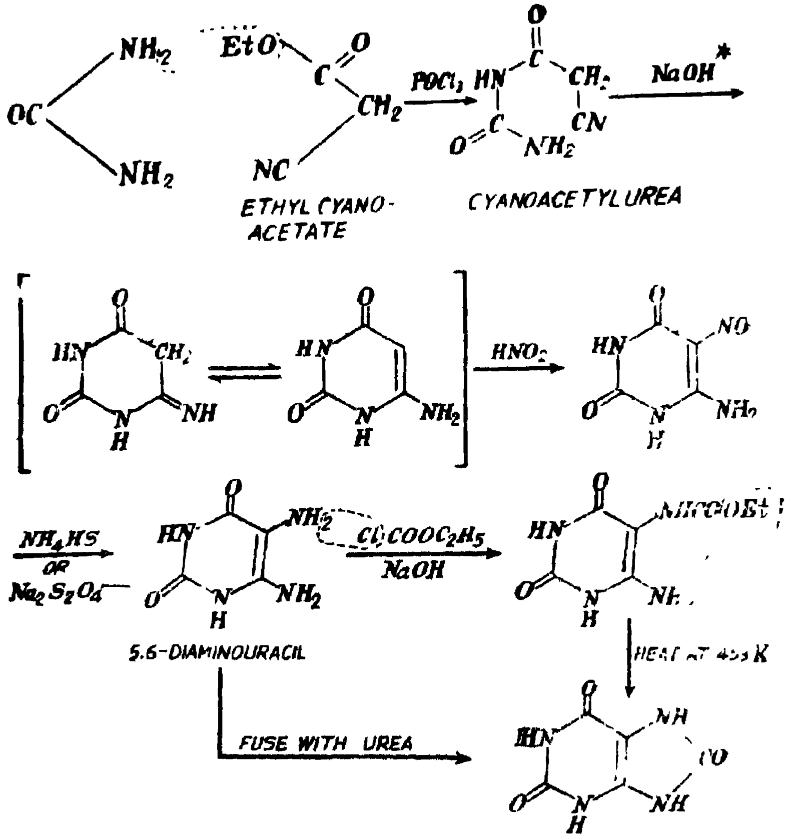
(5) **Acceptance of Medicus formula.** Fischer (1884) prepared two monomethyluric acids ; one gave on oxidation with nitric acid methylalloxan and urea whereas the other one gave alloxan and methylurea.

Fittig's formula, being symmetrical, can give only one monomethyluric acid and is, therefore, untenable.

Medicus formula can give rise to two monomethyl derivatives. One of these has the methyl group in the pyrimidine ring (at position 1 or 3) to give methylalloxan and urea on oxidation. The other one has the methyl group in the imidazole ring (at position 7 or 9) to give alloxan and methylurea on oxidation. Fischer showed these to be 3- and 9-derivatives.

(6) **Further Confirmation of Medicus Formula.** Medicus formula can give four monomethyl derivatives six dimethyl derivatives and four trimethyl derivatives. All of these have been prepared, thus giving a powerful support to this

This formula has been finally confirmed by synthesis of uric acid by Traube in 1900, as shown below :



Tests for Uric Acid. (*i*) It chars on heating, reduces Fehling's solution and decolorises acid or alkaline $KMnO_4$ solution in the cold.

(*ii*) *Murexide Test.* Add concentrated nitric acid to a little uric acid taken in a dish. Evaporate the mixture to dryness on a water-bath and add dilute ammonia. An intense purple colour is obtained due to the formation of murexide. This changes to blue on adding a drop of sodium hydroxide.

8. **Xanthine, 2 : 6-dihydroxypurine, $C_5H_4O_2N_4$.**—Xanthine is present in tea leaves, meat extract and urine. Meat and sprouting

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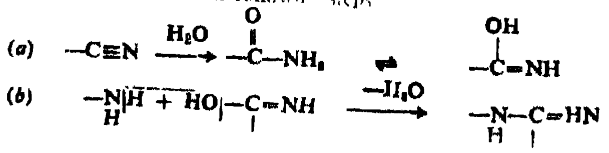
Note. Condensation of —CN group with —NH_2 group resulting in ring closure can be visualised in the following steps



$$(a)\quad -C{\equiv}N \xrightarrow{H_2O} -\overset{\overset{\Large O}{\|}}{C}-NH_2 \rightleftharpoons -\overset{\overset{\large OH}{|}}{C}{=}NH$$

$$(b)\quad -\underset{H}{N}|\overline{H + HO}|-\underset{|}{C}{=}NH \xrightarrow{-H_2O} -\underset{H}{N}-\underset{|}{C}{=}HN$$

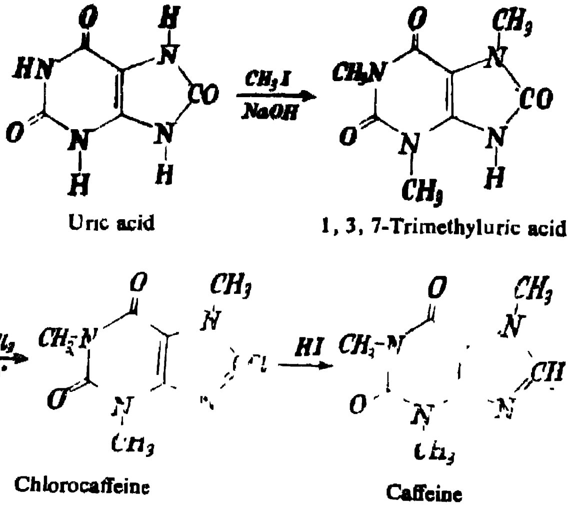
seedlings also contain xanthine. It may be prepared by reduction of uric acid with sodium amalgam.

It is an amorphous powder, very slightly soluble in water but readily dissolves in alkalis. Just like uric acid it yields alloxan and urea on oxidation. It forms salts both with acids as well as bases.

9. **Caffeine, 1, 3, 7-trimethylxanthine, $C_8H_{10}O_2N_4$.**—Caffeine occurs in coffee beans, tea leaves, kola nuts and some other plants.

Preparation : (*i*) *From Tea leaves.* Caffeine is manufactured from damaged tea leaves. Tea leaves are boiled with water and filtered. The filtrate contains caffeine, proteins and tannins. It is treated with basic lead acetate to precipitate proteins and tannins. The precipitates are removed and the filtrate is treated with dilute sulphuric acid to remove excess of lead as insoluble lead sulphate. The precipitate is filtered off and the filtrate decolorised with animal charcoal and caffeine extracted from it with chloroform. The chloroform is distilled off and the residue recrystallized from water.

(*ii*) *Synthesis from Uric Acid.* Caffeine is also manufactured from uric acid which is quite cheap. Uric acid is treated with excess of methyl iodide in alkaline solution when it gives trimethyluric acid. This is heated with phosphoryl chloride to get chlorocaffeine which on reduction with hydriodic acid yields caffeine.



Uric acid

1, 3, 7-Trimethyluric acid

Chlorocaffeine

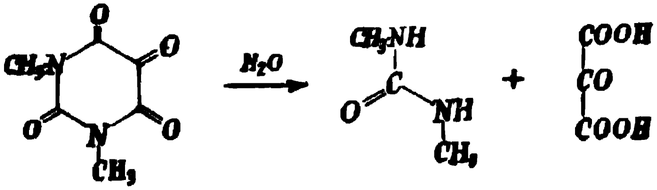
Caffeine

Properties. It crystallizes giving colourless silky needles (with a molecule of water) which melt at 507K. It is fairly soluble in chloroform and alcohol but sparingly soluble in water and ether. On heating, it sublimes and has a bitter taste. It is a weak base and forms salts only with strong acids. Caffeine and its salts stimulate the heart and nerves. It is also an important diuretic. Caffeine gives murexide test like uric acid (*see* page 3·148). India manufactures about 10,000 kg of caffeine every year from damaged tea leaves.

Constitution. (1) Molecular formula of caffeine as deduced from its analytical data is $C_8H_{10}O_2N_4$.

(2) Its relationship with uric acid is shown by the fact that on oxidation with $KClO_3$ in HCl, caffeine gives dimethylalloxan and methylurea in equimolecular proportions.

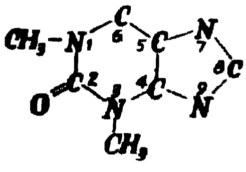
Structure of dimethylalloxan is established by its hydrolysis to *sym*-dimethylurea and mesoxalic acid. It is further confirmed by its synthesis from these compounds.



Dimethylalloxan *sym*-dimethylurea mesoxalic acid

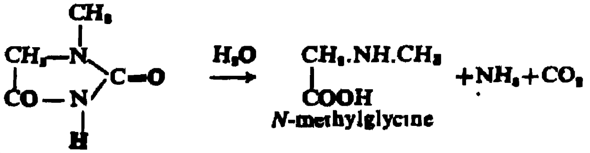
(3) These results indicate that caffeine and uric acid have similar structure. At the same time the positions of two methyl groups and one oxygen atom in caffeine are also established.

(4) Thus the problem now is to ascertain the position of remaining CH_3 group and oxygen atom.



The skeleton structure of caffeine given in the margin summarises the above information. The third methyl group is either at 7 or at 9 position and the remaining oxygen is situated at position 6 or 8.

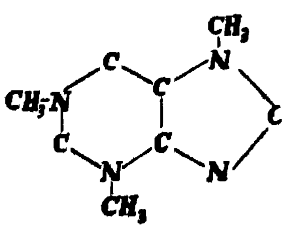
(5) **Position of methyl group.** As stated above caffeine on oxidation gives dimethylalloxan and methylurea. Fischer, however, isolated another product also which on hydrolysis gave *N*-methylglycine, CO_2 and NH_3. Thus the third oxidation product must be *N*-methylhydantoin.



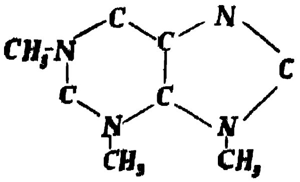
N-methylglycine

N-methylhydantoin

It, therefore, follows that caffeine contains two ring structures, one that of dimethylalloxan and second that of *N*-methylhydantoin. The following two skeleton structures of caffeine are equally possible since each one of these could give the required oxidation products.



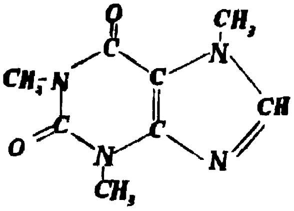
(I)

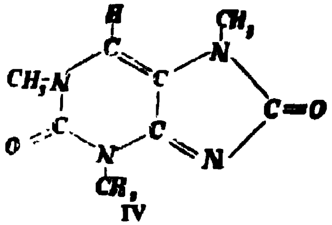


II

Fischer isolated a fourth oxidation product, *viz.*, *sym*-dimethyloxamide, $CH_3.NH.CO.CO.NH.CH_3$. Examination of the skeletons **I** and **II** would show that only **I** can give rise to the formation of this oxamide. Hence **I** is the skeleton of caffeine.

(6) **Position of Oxygen atom.** In view of what has been said above, we see that there are now two possible structures of caffeine (**III** and **IV**) which fit the facts equally well.


III


IV

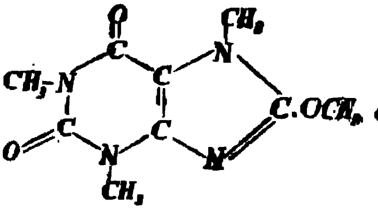
By analogy with uric acid, **III** would appear to be the more likely structure of caffeine. This, however, is not a proof. Fischer showed **III** to be the structure of caffeine as follows :

Caffeine on chlorination gives chlorocaffeine which on treatment with methanol in presence of alkali gives methoxycaffeine. This on boiling with dilute hydrochloric acid yields oxycaffeine and methyl chloride.

$$\underset{\text{Caffeine}}{C_8H_{10}O_2N_4} \xrightarrow{Cl_2} \underset{\text{Chlorocaffeine}}{C_8H_9O_2N_4Cl} \xrightarrow[NaOH]{CH_3OH} \underset{\text{Methoxycaffeine}}{C_8H_9O_2N_4.OCH_3}$$

$$\xrightarrow[\text{boil}]{\text{dil.HCl}} \underset{\text{Oxycaffeine}}{C_8H_{10}O_3N_4} + CH_3Cl$$

Fischer then showed that *oxycaffeine was identical with a trimethyluric acid*, since on methylation with CH_3I in presence of aqueous NaOH, oxycaffeine was converted into tetramethyluric acid. This methoxycaffeine is either **V** or **VI** and oxycaffeine is either **VII** or **VIII**.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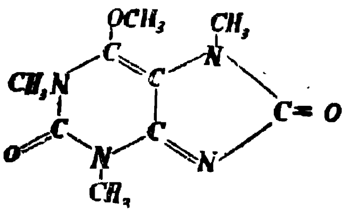
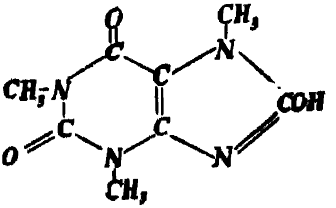

V Methoxycaffeine VI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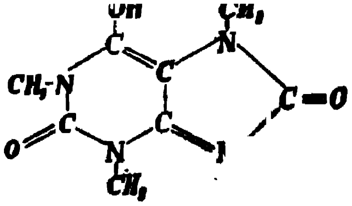

VII Oxycaffeine VIII

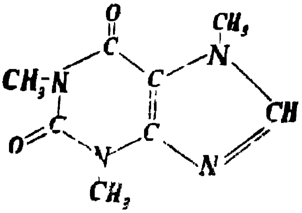
When silver salt of oxycaffeine is heated with methyl iodide, it is converted into a mixture of tetramethyluric acid (which contains four *N*-methyl groups) and methoxycaffeine (which contains three *N*-methyl groups and one methoxy group).

This simultaneous formation of these two products suggests that oxycaffeine is a tautomeric substance, *i.e.*, it contains the amido-imidol triad system.

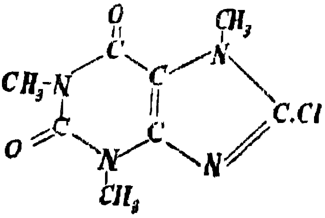
$$-NH-\overset{|}{C}=O \rightleftharpoons -N=\overset{|}{C}-OH$$

This triad system can exist only in the imidazole nucleus in oxycaffeine, since neither nitrogen atom in the pyrimidine nucleus is attached to a hydrogen atom. Examination of structures **VII** and **VIII** shows that **VII** can give rise to the above tautomeric system whereas **VIII** cannot.

Thus the methoxy group in methoxycaffeine is in the imidazole nucleus and consequently the chlorine atom in chlorocaffeine is also in this nucleus. Hence caffeine is **IX** and chlorocaffeine is **X**.



(IX) Caffeine



(X) Chlorocaffeine

This structure has been finally confirmed by its synthesis as given on page 3·149.

10. **Theobromine, 3, 7-dimethylxanthine.**—It occurs in cocoa beans. It is a white crystalline solid (m.p. 624K) with slightly bitter taste. It is readily soluble in water and finds use in medicine as diuretic.

11. **Adenine, 6-aminopurine.**—It occurs in tea leaves, molasses, yeast and urine. It is manufactured from tea and molasses.

It is a colourless solid (m.p. 633K) highly soluble in water. It dissolves in acids and alkalis forming salt with them.

12. **Guanine, 2-amino-6-hydroxypurine.**—Along with adenine, it occurs in many plants and in the organs of animals, *e.g.*, skin and scales of fish and reptiles.

It is a colourless solid very nearly insoluble in water and alcohol. It dissolves in acids and alkalis due to the formation of salts.

13. **Hypoxanthine, Sarkine, 6-hydroxypurine.**—It is present in muscles, spleen, liver and pancreas. It is a crystalline powder which decomposes when heated at 423K without melting. It is slightly soluble in water but dissolves in alkalis due to the formation of salts with them.

QUESTIONS

Essay Type :

1. What are ureides and purines ? How are they related ? *(Delhi B.Sc. Hons. 1974)*

2. How is uric acid obtained ? Discuss its chemistry and show its relationship to caffeine and theobromine.

3. How is uric acid synthesised ? Discuss its constitution. *(Guru Nank B.Sc. 1971 ; Delhi B.Sc. Hons. 1975, 73)*

4. Discuss the constitution of uric acid. How is it converted into caffeine and purine ? *(Utkal B.Sc. 1976 ; Delhi B.Sc. Hons. 1975, 73, 72)*

5. How would you prepare caffeine ? What are its chief uses ?

6. Discuss the evidence both analytical and synthetical on which the structure of caffeine is based. *(Delhi B.Sc. Hons. 1974)*

7. How is caffeine prepared ? Describe its important properties and uses.

8. How is veronal prepared ? Mention its important uses.

9. Uric acid, $C_5H_4O_3N_4$ on oxidation with alkaline permanganate yields allantoin, $C_4H_6O_3N_4$ and CO_2. Discuss how the structure of allantoin is derived. Write the structural formula of uric acid. *(Delhi B.Sc. Hons. 1978)*

10. Why, in ureides, is the N—H bond quite acidic in character and can easily be replaced by an alkyl group on treating the ureide with metals and alkyl halides ? *(Delhi B.Sc, Hons. 1978)*

Short Answer Type :

1. What are ureides ? How are they classified ?

2. Write names and formulae of products obtained in the following reactions :

(*i*) Acetamide + $COCl_2$ → (*ii*) Oxalic acid + urea →

(*iii*) Malonic ester + urea → (*iv*) Glycollic acid + urea →

(*v*) Acetoacetic ester + urea →

3. Write structural formulae of the following :

(*i*) Veronal (*ii*) Luminal (*iii*) Bromural

4. Write structural formula of pyrimidine. How is it obtained from barbituric acid ?

5. Write canonical forms of the resonance hybrid of pyrimidine.

6. Write structures of—

(*i*) Pyrimidine ring ; (*ii*) Imidazole or iminazole ring ; (*iii*) Purine.

7. How is uric acid converted into purine ? *(Delhi B.Sc. Hons. 1976)*

8. How are the following related to each other ?

(*i*) Uric acid ; (*ii*) Xanthine ; (*iii*) Caffeine. *(Delhi B.Sc. Hons. 1976)*

9. Write structural formulae of

(*i*) Alloxan ; (*ii*) Allantoin ; (*iii*) Uric acid.

10. What happens when allantoin is treated with the following :

(*i*) HNO_3 ; (*ii*) Alkali ; (*iii*) HI

11. Starting from cyanoacetic ester how would you synthesise uric acid ? *(Delhi B.Sc. Hons. 1976)*

12. Write structural formula for—

(*i*) Caffeine ; (*ii*) Dimethylalloxan ; (*iii*) *N*-methylhydantoin.

8

Alkaloids

1. Introduction.—Alkaloids (*Alkali-like* substances) cannot be defined precisely by any brief statement because this term is applied to a large group of complex and rather loosely-related compounds. These are now generally defined as *basic nitrogenous compounds of vegetable origin usually having a marked physiological action and which may be regarded as derived from pyrrole, pyridine, quinoline, isoquinoline or similar cyclic nitrogenous nuclei.* Many of them possess curative properties and are of great value in medicine.

Pharmacists often include caffeine and theobromine among the alkaloids because of their basicity. Their chemical structure, however, places them with the purines and the purine bases are not usually classed among the alkaloids.

Although the poisonous and therapeutic properties of various plants have been known and utilised from early times, the first alkaloid (morphine) was isolated by Serturner only in 1817 from opium. This was followed by the discovery of strychnine (1818), brucine (1819), quinine (1820) and many other alkaloids. All attempts to determine their constitutions or to prepare them synthetically, however, failed for a long time.

Their common basic character was suggested by Liebig to be due to the presence of nitrogen. It was later found that pyridine and other heterocyclic bases were obtained from alkaloids by drastic treatment with caustic alkali, zinc dust, etc. Important work on synthesis and constitution of alkaloids was carried on from 1870 onwards by Ladenburg, Skraup, Konigs, Pschori, Willstatter, Pictet, Perkin (Junior), Robinson and others.

2. Occurrence.—Alkaloids are usually found in plants (generally of the class of dicotyledons) in the form of salts—in which they are either combined with organic acids such as lactic, citric, malic, oxalic, commonly found in plants or with certain characteristic acids such as quinic acid (in cinchona alkaloid) and meconic acid. In some cases they exist as glycosides. Although they may be detected in all parts of the plant, they generally accumulate in the fruit and seeds and also in the bark of trees.

3. Extraction of Alkaloids from Plants.—The plant material is finely powdered and treated with water acidified with hydrochloric or sulphuric acid when the alkaloids form salts with these mineral acids and dissolve in water. The water extract contains the hydrochlorides or sulphates of alkaloids together with dyestuffs, carbohydrates and other products from the plant tissue. This is treated with alkali when the alkaloids (being sparingly soluble in water) are precipitated. In the case of volatile alkaloids, the acidulated water extract is treated with alkali and steam-distilled.

Purification of the crude product obtained above is carried on by special methods or frequently by crystallization of the freed compounds or their salts.

4. General Properties.

(*i*) *State.* Most of the alkaloids are crystalline solids which cannot be distilled. Only a few of them are liquids and volatilize without decomposition, *e.g.*, coniine and nicotine.

(*ii*) *Physiological action.* Most of them are bitter in taste and often exert a marked physiological action.

(*iii*) *Solubility.* Almost all of them are either insoluble or sparingly soluble in water. Liquid alkaloids (coniine and nicotine) are notable exceptions (being readily soluble in water and appreciably volatile in steam). Alkaloids dissolve with more or less difficulty in chloroform, ether and benzene but are readily soluble in alcohol.

(*iv*) *Optical activity.* Most of them are optically active and usually laevo-rotatory.

(*v*) *Basic nature.* In a number of cases their solutions give a strong alkaline reaction. All of them form salts with acids. Among these salts the chlorides, sulphates and oxalates crystallize well. Their chlorides give double salts with chlorides of gold, platinum and mercury.

(*vi*) *Precipitation.* Alkaloids are precipitated from their aqueous or acid solution by a number of substances called (*alkaloid reagents*) such as picric acid, tannic acid, perchloric acid, potassium mercuric iodide, potassium bismuth iodide, phosphomolybdic acid and phosphotungstic acid. Precipitation with alkaloid reagents is often employed for the isolation and purification of alkaloids. This cannot, however, be used for quantitative analysis since the resulting compounds are not sufficiently insoluble and because the reagents precipitate some other organic substances also.

5. Determination of the Chemical Constitution of Alkaloids.—Different steps involved in the determination of constitution of an alkaloid are :

(*a*) **Determination of Molecular Formula.** The specimen is purified and subjected to qualitative analysis. Carbon, hydrogen and nitrogen are invariably present while oxygen is rarely absent. This is followed by quantitative analysis, determination of molecular weight and then calculation of empirical and molecular formulae.

(*b*) **Detection of Groups.** Knowing the presence of nitrogen and/or oxygen in the alkaloid, the functional nature of these elements is determined.

FUNCTIONAL NATURE OF OXYGEN

(1) *Hydroxyl group.* The alkaloid is treated with acetic anhydride, acetyl chloride or benzoyl chloride to detect the presence of hydroxyl group. (Note that Amino group also reacts with these reagents.)

The hydroxyl group may be phenolic or alcoholic. It is phenolic if the alkaloid—

(*i*) gives a coloration with ferric chloride ;

(*ii*) is soluble in sodium hydroxide and is reprecipitated by carbon dioxide.

If the hydroxyl group is not phenolic, it must be alcoholic. This is confirmed by treatment with dehydrating agents (H_2SO_4 and P_4O_{10}) or by oxidation.

(2) *Carboxyl group*. Presence of a carboxyl group is indicated by the solubility of the alkaloid in aqueous sodium carbonate or formation of esters.

(3) *Ester group*. Identification of the products of hydrolysis of the alkaloid indicates presence or absence of an ester group.

(4) *Methoxy group*. The presence of methoxy groups and their number is determined by Zeisel method described under Estimation of Groups.

FUNCTIONAL NATURE OF NITROGEN

(5) *Amino Group*. (*i*) The reactions of the alkaloid with acetic anhydride, benzoyl chloride, nitrous acid and methyl iodide show whether the amino group is primary, secondary or tertiary.

(*ii*) Formation of methylamine, dimethylamine, trimethylamine (volatile products) on distillation with aqueous potassium hydroxide indicates the nature and number of methyl groups attached to nitrogen atom.

(6) *Amide group*. Products of hydrolysis (acid and ammonia) the alkaloid will show the presence of amide group.

(7) *Presence of Unsaturation*. Presence of unsaturation is indicated by treatment with bromine water or dilute alkaline permanganate. Reduction with sodium amalgam, sodium and alcohol, hydriodic acid or tin and hydrochloric acid also show the presence of unsaturation.

(*c*) **Estimation of Groups**. The estimation of various groups detected as above, is carried on as follows :

(1) *Hydroxyl groups*. The number of hydroxyl groups is determined by acetylating the alkaloid followed by hydrolysis of the acetyl derivative with a known volume of N-NaOH. The excess of the alkali left unused is estimated by back titration with a standard acid.

$$\underset{\substack{\text{Hydroxy}\\\text{compound}}}{ROH}\xrightarrow{CH_3COCl}\underset{\text{Acetyl deriv}}{RO.OCCH_3}\xrightarrow{NaOH}ROH+CH_3COONa$$

From the volume of N-NaOH used, the number of acetyl groups or hydroxyl groups can be calculated.

(2) *Carboxyl groups*. The number of carboxyl groups may be determined volumetrically by titration against a standard barium hydroxide solution using phenolphthalein as indicator or gravimetrically by silver salt method.

(3) *Methoxy groups.* The presence of methoxy groups and their number may be determined by the *Zeisel method.* The alkaloid is heated with concentrated hydriodic acid at 399K, boiling point of HI. The methoxy groups present in the molecule are thereby changed into methyl iodide which is absorbed in alcoholic silver nitrate when silver iodide is precipitated.

$$R(OCH_3)_x + xHI \longrightarrow R(OH)_x + xCH_3I$$
$$xCH_3I + xAgNO_3 \longrightarrow xAgI + xCH_3NO_3$$

The precipitate of AgI is boiled with HNO_3, filtered, washed, dried and weighed.

From the weight of silver iodide, we calculate the number of methoxy groups as illustrated in the solved example given below :

Example 1. *When treated according to Zeisel's method 0·226 gram of an alkaloid $C_{20}H_{21}O_4N$ yielded 0·626 gram of silver iodide. Calculate the number of methoxy groups present in the molecule of the alkaloid.*

Solution.

Mol. mass of the alkaloid, $C_{20}H_{21}O_4N = 240+21+64+14 = 339$
Wt of alkaloid taken $= 0·226$ g.
Wt of AgI obtained $= 0·626$ g.

∴ The wt of AgI that will be produced by 1 mole, *i.e.*, 339 g of alkaloid $= \frac{0·626}{0·226} \times 339 = 939$ g.

Mol mass of AgI $= 107·88 + 127 = 234·88$.

It is clear from the equations given above that corresponding to each methoxy group present, one molecule of AgI is obtained at the end. Hence the number of methoxy groups in the molecule of the alkaloid $= \frac{939}{234·88} = 4$.

(*d*) **Degradation.** The complex molecule is broken into relatively simple fragments nature of which gives useful information about the type of nuclei present in the molecule. Various methods employed for degradation are :

(1) *Hydrolysis.* Molecules containing an ester or amide group break on hydrolysis into simpler products. For example, piperine on hydrolysis splits up to give piperic acid and piperidine.

$$\underset{\text{Piperine}}{C_{11}H_9O_2CO{-}NC_5H_{10}} + H_2O \longrightarrow \underset{\text{Piperic acid}}{C_{11}H_9O_2COOH} + \underset{\text{Piperidine}}{C_5H_{10}NH}$$

From this we infer that piperine is a piperidinamide of piperic acid.

(2) *Oxidation.* Alkaloids on oxidation give a variety of products depending upon the nature of oxidising agents—mild (H_2O_2 or alkaline potassium ferricyanide), moderate (acid or alkaline $KMnO_4$) or vigorous ($K_2Cr_2O_7 + H_2SO_4$; conc. HNO_3 or $MnO_2 + H_2SO_4$)

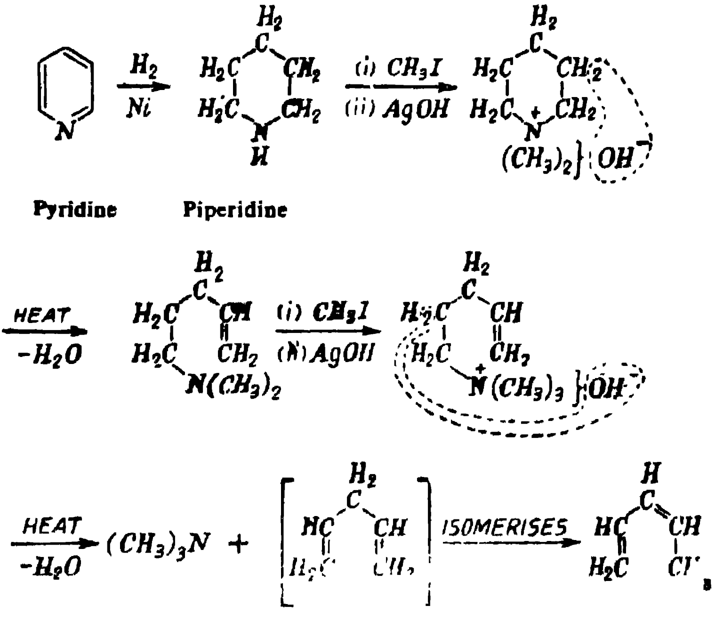
(3) *Distillation with Zinc dust.* This brings about degradation or dehydrogenation. When the alkaloid contains oxygen it is removed during distillation. For example, on distillation with zinc

dust morphine yields phenanthrene (parent compound) while coniine undergoes dehydrogenation to give conyrine.

(4) *Exhaustive Methylation*. Heterocyclic rings containing nitrogen are opened with the elimination of nitrogen when subjected to exhaustive methylation. It thus helps us in knowing the nature of the carbon skeleton.

The heterocyclic compound is hydrogenated, if unsaturated, and converted to the quaternary methylammonium hydroxide. This on heating loses a molecule of water by combination of —OH group with a hydrogen atom in β-position with respect to the nitrogen atom and the ring is opened at the nitrogen atom.

On repeating the process with the product, nitrogen atom is completely removed leaving an unsaturated hydrocarbon behind which generally isomerises to a conjugated diene. For example, starting with pyridine we have



Pyridine Piperidine

Piperylene

(*e*) **Synthesis**. The alkaloid under investigation is assigned a tentative structure on the basis of the foregoing analytical data. This is finally proved only if it could be synthesised by suitable methods.

SOME INDIVIDUAL MEMBERS

6. **Coniine**, $C_8H_{17}N$.—Coniine is one of the simple alkaloids. It is found in the seeds and other parts of the spotted hemlock (*Conium maculatum*), a shrub growing in wet locations. Socrates, the Greek philosopher who was condemned to death in 399 B.C. for his

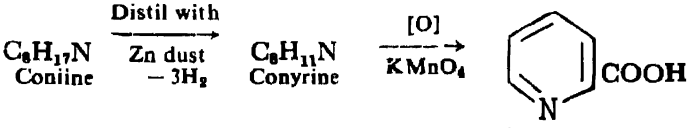
crime of teaching the young to think, was forced to drink hemlock extract. It was the first alkaloid to be synthesised (by Ladenburg in 1886) and thus the alkaloid which was responsible for causing the death of the wisest of men was the first to succumb to the synthetic skill of the organic chemist.

Coniine is isolated from the powdered hemlock seeds by distilling with caustic soda solution. The distillate contains coniine which is extracted with ether. The ethereal extract is evaporated when the alkaloid is left behind as an oily residue.

Properties. It is a colourless oil which boils at 439-440K. It is optically active, the natural product being dextrorotatory having specific rotation = +15·7°. It has an unpleasant smell and turns brown on exposure to air. It is soluble in water but more soluble in alcohol. Coniine as well as its salts are exceedingly poisonous and cause death by paralysis of the motor nerve endings and depression of the central nervous system.

Constitution. (1) The molecular formula of coniine as deduced from its analytical data and molecular weight determination is $C_8H_{17}N$.

(2) When distilled with zinc dust coniine is converted into conyrine ($C_8H_{11}N$) which on oxidation with permanganate gives 2-pyridinecarboxylic acid (α-picolinic acid).



2-Pyridine-carboxylic acid

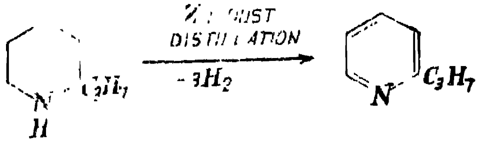
This shows that—

(*i*) In conyrine a pyridine nucleus is present with a side-chain in the 2-position.

(*ii*) Conyrine (having a pyridine nucleus) is formed when coniine loses six hydrogen atoms on zinc dust distillation. Thus coniine is probably a piperidine derivative with a side-chain in 2-position.

(*iii*) Coniine and piperidine being $C_8H_{17}N$ and $C_5H_{10}N$ respectively, the above side-chain must be C_3H_7 (their difference), propyl radical.

Thus the formulae of coniine and conyrine can be written as follows :

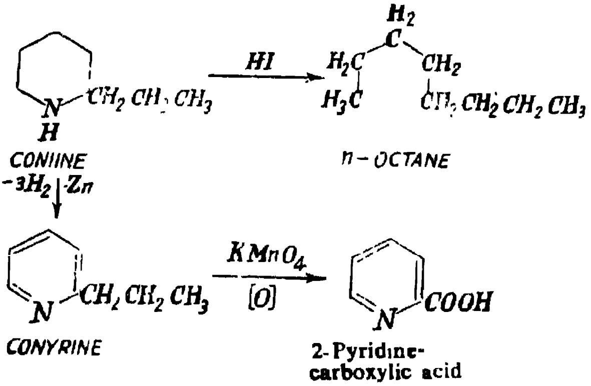


Coniine Conyrine

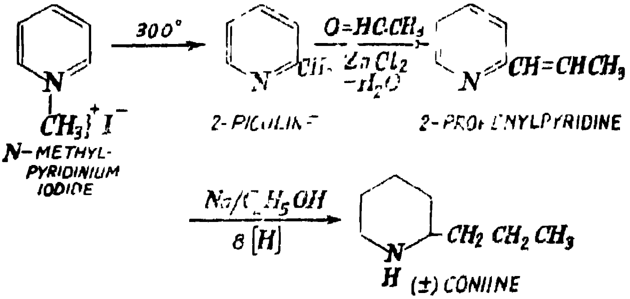
(3) The propyl group constituting the side-chain may be *n*-propyl or isopropyl. On heating with hydriodic acid at 570K under pressure, coniine gives *n*-octane. This shows that the side-chain is

n-propyl and not isopropyl. Had it been isopropyl, the expected product would have been isooctane.

This shows that coniine is 2,n-propylpiperidine and various reactions of coniine described above can be formulated as follows:

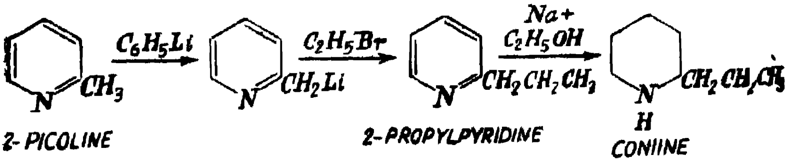


(4) This has been further confirmed by synthesis (Ladenburg, 1885). N-methylpyridinium iodide on heating to 570K (300°C) gives 2- and 4-methylpyridines. 2-Picoline (2-methylpyridine) condenses with acetaldehyde at 520K to form 2-propenylpyridine. This on reduction with sodium and alcohol gives coniine.



Coniine so synthesised is a racemic mixture and is resolved by forming salts with (+) tartaric acid. The salt of (+) coniine being less soluble, crystallizes out first. This on treatment with alkali gives (+) coniine which is found to be identical with the natural compound.

Coniine has also been synthesised by Bergmann (1932) from 2-methylpyridine and phenyllithium as follows :



7. **Piperine,** $C_{17}H_{19}O_3N$.—Piperine occurs in pepper, especially black pepper (Piperine nigrum) to the extent of 7 to 9 per cent.

It was first prepared by Oersted in 1819 and crystallizes in monoclinic crystals (m.p. 401-402·5K) having the flavour and taste of black pepper. It is sparingly soluble in water and is much less toxic than other alkaloids.

Constitution. (1) Molecular formula of piperine as deduced from its analytical data and molecular weight determination is $C_{17}H_{19}O_3N$.

(2) Hydrolysis of piperine by boiling with alcoholic potash gives piperidine and piperic acid.

$$\underset{\text{Piperine}}{C_{17}H_{19}O_3N}+H_2O \xrightarrow[\text{KOH}]{\text{Alc.}} \underset{\text{Piperidine}}{C_5H_{10}NH}+\underset{\text{Piperic acid}}{C_{11}H_9O_2.COOH}$$

This shows that piperine is piperidine amide of piperic acid. We know that piperidine is hexahydropyridine and if the structure of piperic acid could be elucidated, the constitution of the alkaloid will be known

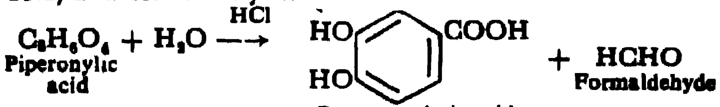
(3) **Structure of piperic acid.** (*i*) Routine tests indicate the presence of one carboxyl group and two double bonds in piperic acid.

(*ii*) Piperic acid ($C_{11}H_9O_2$.COOH) on oxidation with permanganate gives first piperonal and then piperonylic acid, $C_7H_5O_2$.COOH which has 4 carbon and 4 hydrogen atoms less than the parent acid.

Change of piperonal to piperonylic acid involves change of aldehydic group (—CHO) to carboxyl group (—COOH).

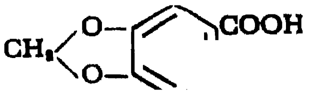
$$\underset{\text{Piperic acid}}{C_{11}H_9O_2COOH} \xrightarrow[\text{KMnO}_4]{O} \underset{\text{Piperonal}}{C_7H_5O_2.CHO} \xrightarrow[\text{KMnO}_4]{O} \underset{\text{Piperonylic acid}}{C_7H_5O_2.COOH}$$

(*iii*) On heating with hydrochloric acid at 470K under pressure piperonylic acid forms protocatechuic acid (3 : 4-dihydroxybenzoic acid) and formaldehyde.



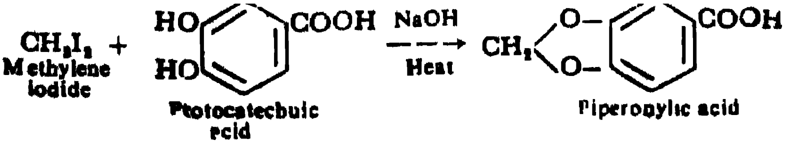
Protocatechuic acid

Since there are no free hydroxyl groups in piperonylic acid and in the above conversion it loses only one carbon atom, it suggests that piperonylic acid is probably the methylene ether of protocatechuic acid, *i.e.*, it is 3 : 4-methylenedioxybenzoic acid.

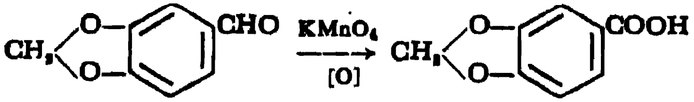


Piperonylic acid or
3 : 4-methylenedioxybenzoic acid

(*iv*) This structure of piperonylic acid is further confirmed by its synthesis from protocatechuic acid and methylene iodide.



(*v*) Further since piperonal is an aldehyde which gives piperonylic acid on oxidation, it must be 3 : 4 methylenedioxybenzaldehyde.

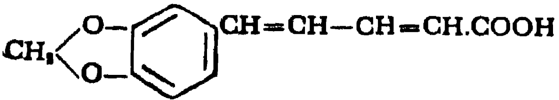


Piperonal Piperonylic acid

(*vi*) These oxidation products (piperonal and piperonylic acid) suggest that piperic acid is a benzene derivative containing only side-chain. The two double bonds (shown by ready addition of four bromine atoms) must be present in this side chain.

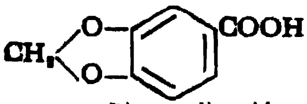
Further since piperic acid on careful oxidation yields tartaric acid in addition to piperonal and piperonylic acid, the side-chain must be a *straight-chain*.

(*vii*) Hence formula of piperic acid containing 3 : 4-methylenedioxybenzene ring, a side-chain containing two double bonds, a carboxylic group with the carbon atoms arranged in straight-chain, can be written as



Piperic acid

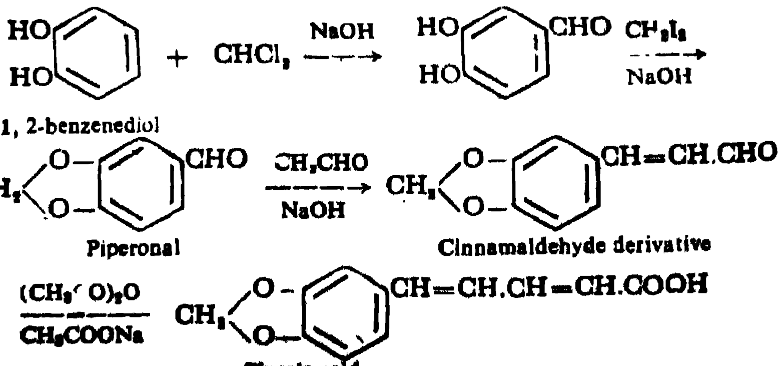
which on oxidation gives



and HOOC.CHOH.CHOH.COOH

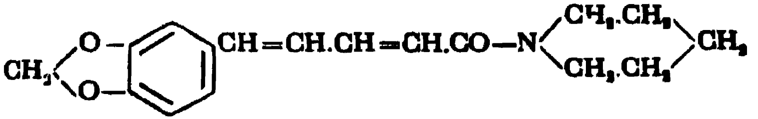
Piperonylic acid Tartaric acid

(*viii*) The structure of piperic acid has been confirmed by its synthesis by Ladenburg in 1894. Piperonal is prepared from 1, 2-benzenediol *via* Reimer-Tiemann reaction. This is condensed with acetaldehyde in presence of caustic soda (Claisen-Schmidt reaction). The condensation product, a cinnamaldehyde derivative, is then heated with a mixture of acetic anhydride and sodium acetate (Perkin reaction) when piperic acid is obtained.

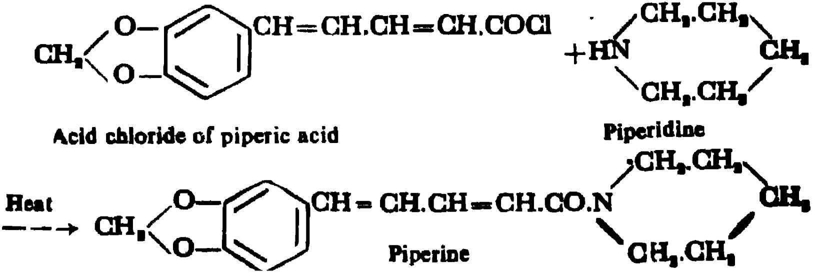


1, 2-benzenediol Piperonal Cinnamaldehyde derivative Piperic acid

(4) Structural formula of piperine as piperidine amide of piperic acid can be written as



(5) This structure is confirmed by its synthesis from the acid chloride of piperic acid (obtained by the action of PCl_5 on the acid). The acid chloride is heated with piperidine in benzene solution when piperine is obtained.



Acid chloride of piperic acid

Piperidine

Piperine

8. **Nicotine, $C_{10}H_{14}N_2$.**—It is the chief alkaloid of the tobacco plant (*Nicotiana tobacum*) wherein it is present as a salt of malic or citric acid. In leaves of tobacco its concentration is the highest. It varies from 0·6 to 8% depending upon the kind of tobacco.

The alkaloid is conveniently prepared from tobacco leaves. Raw tobacco of high nicotine content is crushed and its soluble constituent extracted with cold water. The hydrocarbons present in the extract are removed by acidifying the solution and extracting with ether. The residual solution is made alkaline and nicotine set free is extracted with ether.

Properties. Freshly prepared nicotine is a colourless oily liquid (b.p. 519·2K under 730 mm pressure) readily soluble in water. Pure nicotine has an unpleasant smell unlike that of tobacco. It has a burning taste and is very poisonous (lethal dose being 30 to 50 mg). In air it rapidly turns brown and resinifies and can be distilled without decomposition only in vacuum or in a current of hydrogen. The natural alkaloid is laevo-rotatory $[\alpha]_D = -169°$.

In admixture with soap solution it is one of the most effective exterminating agents for green fly and other insect pests.

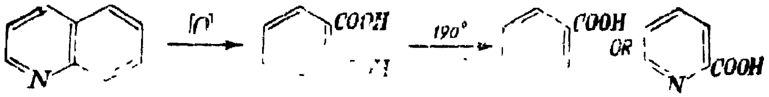
Constitution. (1) Molecular formula of nicotine as deduced from its analytical data and molecular mass determination is $C_{10}H_{14}N_2$.

(2) Nicotine reacts with methyl iodide to form dimethiodide and two monomethiodides but it does not form an acetyl or benzoyl derivative. This shows that the two nitrogen atoms in nicotine are tertiary.

(3) Nicotine on oxidation with chromic acid or permanganate gives nicotinic acid ($C_5H_4N.COOH$). Three pyridinecarboxylic acids

are known with COOH group in 2-, 3- or 4- position. These ar named picolinic acid, nicotinic acid and isonicotinic acid. Th orientation was proved as follows :

Quinoline on oxidation with alkaline permanganate gives quin linic acid which must be 2, 3-pyridinedicarboxylic acid. Quinolin acid on being heated to 360K loses one carboxyl group and gives nic tinic acid. Hence nicotinic acid must be either 2-pyridinecarboxyl acid or 3-pyridinecarboxylic acid.



Quinoline

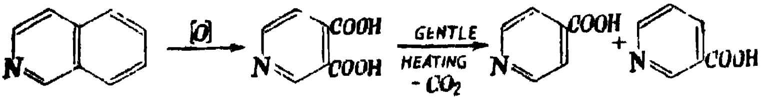
Quinolinic acid (2, 3-pyridinedicarboxylic acid)

3-pyridinecarboxylic acid

2-pyridine carboxylic acid

(Nicotinic acid)

Isoquinoline on oxidation with alkaline permanganate produces cinchomeronic acid which must be 3, 4-pyridinedicarboxyli acid. This, on gentle heating, gives a mixture of nicotinic and iso nicotinic acids. So nicotinic acid is either 3-pyridinecarboxylic aci or 4-pyridinecarboxylic acid.



Isoquinoline

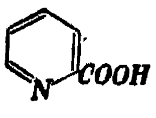
Cinchomeronic acid (3, 4-pyridine-dicarboxylic acid)

4-pyridine-carboxylic acid

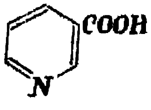
3-Pyridine-carboxylic acid

(Nicotinic and isonicotinic acids)

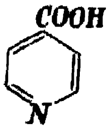
In the above we find that both quinoline and isoquinoline yield nicotinic acid and 3-pyridinecarboxylic acid is a common product in both these reactions, this must be the formula of nicotinic acid. If this is so, then isonicotinic acid must be 4-pyridinecarboxylic acid. By elimination, therefore, piculinic acid is 2-pyridinecarboxylic acid.



Picolinic acid



Nicotinic acid

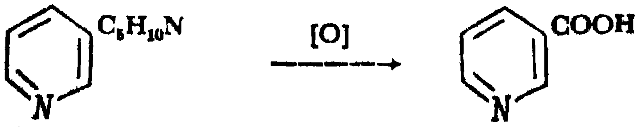


Isonicotinic acid

Now since nicotine on oxidation followed by heating at 460K yields nicotinic acid (3-pyridinecarboxylic acid), it suggests that nicotine contains a pyridine ring with some sort of group attached to it at the β-position. This group attached to pyridine ring is

$$C_{10}H_{14}N_2 - C_5H_4N = C_5H_{10}N$$

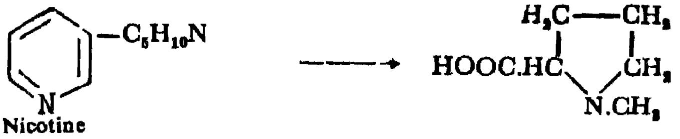
and the oxidation can be formulated as follows :



Nicotine

Nicotinic acid

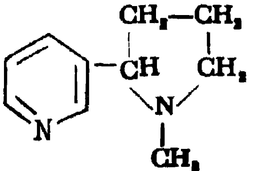
(4) Nicotine hydriodide on treatment with methyl iodide gives a methiodide. This on oxidation yields hygrinic acid (*N*-methylpyrrolidine-α-carboxylic acid). This indicates the presence of pyrrolidine ring with a methyl group attached to N-atom and carrying some other group in 2-position. The transformation can be indicated as follows :



(Mol. formula $C_5H_{10}.N.COOH$)
Hygrinic acid

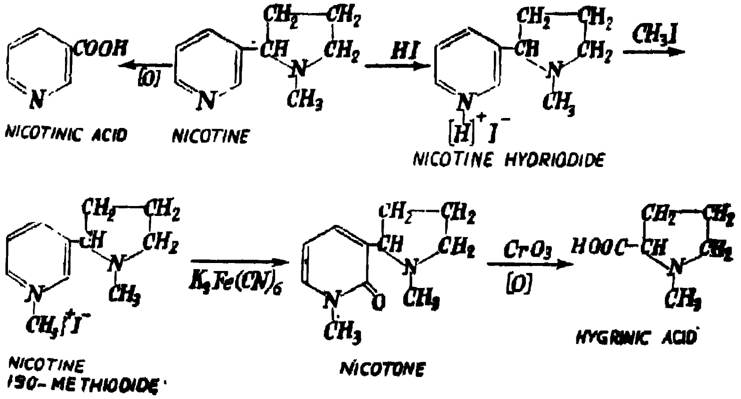
This indicates that pyridine ring has been destroyed during the transformation and the group $—C_5H_{10}N$ attached to the pyridine ring in β-position is *N*-methylpyrrolidine.

(5) Pyridine and pyrrolidine nuclei are joined through carbon atoms at β-position in pyridine and 2-position in pyrrolidine. This gives the structure of nicotine as

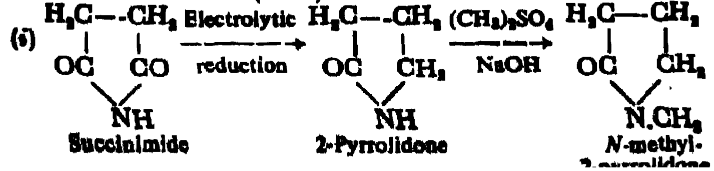


Nicotine (1-methyl-2-β-pyridylpyrrolidine)

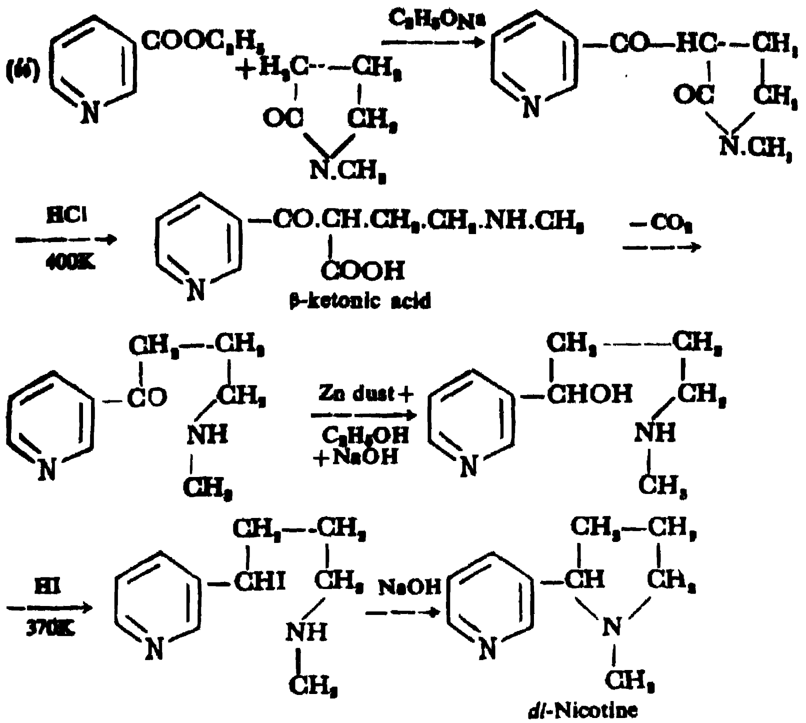
(6) The conversion of nicotine into nicotinic acid and hygrinic acid has been formulated as under :



(7) This formula has been further confirmed by its synthesis by Spath and Bretschneider (1928) as follows :



(ii)



The (±)-mixture was resolved by means of (±)-tartaric acid and (−)-nicotine thus obtained was found to be identical with the natural product.

9. Atropine, $C_{17}H_{23}O_3N$.—Atropine (m.p. 391K) along with *hyosyamine* occurs in deadly nightshade (*Atropa belladonna*) and thorn-apple (fruits of *dhatura stramonium*)—plants of the Solanaceae family.

It has a sharp bitter taste and is extremely poisonous. It has a property of dilating the pupil of the eye and on this account finds an extensive use in eye-surgery.

Constitution. (i) Molecular formula of atropine as deduced from its analytical data and molecular weight determination is $C_{17}H_{23}O_3N$.

(2) Atropine occurs together with hyosyamine. Hyosyamine is optically active and on warming with ethanolic alkali solution racemises to atropine. Thus atropine is (±) hyosyamine.

(3) Atropine undergoes hydrolysis, when warmed with barium hydroxide solution, to give (±) tropic acid and tropine (an alcohol). This suggests that atropine is the tropine ester of tropic acid

$$\underset{\text{Atropine}}{C_{17}H_{23}O_3N} + H_2O \xrightarrow{Ba(OH)_2} \underset{\text{Tropic acid}}{C_9H_{10}O_3} + \underset{\text{Tropine}}{C_8H_{15}ON}$$

(4) Constitution of Tropic acid.

(*i*) Its molecular formula as deduced from its analytical data and molecular weight determination is $C_9H_{10}O_3$.

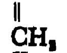
(*ii*) It does not decolorise bromine water, showing it to be a saturated compound.

(*iii*) It shows the presence of one carboxyl group and one alcoholic group from usual tests.

(*iv*) Tropic acid loses a molecule of water, when heated strongly, and gives atropic acid with molecular formula, $C_9H_8O_2$. This on oxidation gives benzoic acid. This suggests that tropic and atropic acids both contain a benzene ring with a side chain. Possible structural formula of atropic acid could, therefore, be either I or II.

$C_6H_5.CH{=}CH.COOH$

I

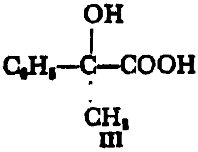


$C_6H_5{-}C(=CH_2){-}COOH$

II

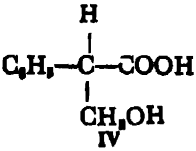
But I is known to be structural formula of cinnamic acid. Hence II is the structural formula of atropic acid.

(*v*) Atropic acid is the dehydration product of tropic acid. Hence structural formula of tropic acid can be written by adding a molecule of water to atropic acid. It can be either III or IV.



$C_6H_5{-}C(OH)(CH_3){-}COOH$

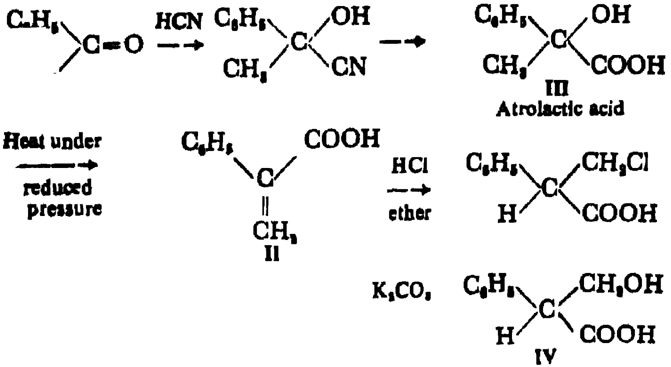
III



$C_6H_5{-}CH(CH_2OH){-}COOH$

IV

(*vi*) Mackenzie and Wood (1919) synthesised tropic acid starting from acetophenone and showed that its structure was IV.



III is the structural formula of atrolactic acid. Its dehydration to II confirms the structural formula of atropic acid. Addition of HCl to II takes place contrarv to Markownikoff's rule due to the inductive effect of COOH group. Tropic acid is optically active and race micvariety is obtained in the above synthesis.

(5) Constitution of Tropine (Tropanol) : (*i*) Molecular formula of tropine as calculated from its analytical data is $C_8H_{15}ON$.

(*ii*) It behaves like a saturated compound which contains an alcoholic group.

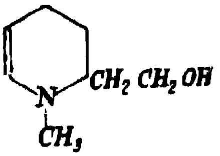
(*iii*) Ladenburg showed the presence of a reduced pyridine nucleus in tropine as follows :

$$\underset{\text{Tropine}}{C_8H_{15}ON} \xrightarrow[\text{(below 420 K)}]{HI} \underset{\text{Tropine iodide}}{C_8H_{14}NI} \xrightarrow{[H]} \underset{\substack{\text{Dihydrotropidine} \\ (\textit{tropane})}}{C_8H_{15}N}$$

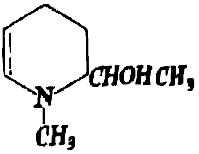
$$\xrightarrow[\text{hydrochloride}]{\text{distil}} CH_3Cl + \underset{\substack{{}^*\textit{nor}\ \text{Dihydro-} \\ \text{tropidine}}}{C_7H_{13}N} \xrightarrow[\text{distil}]{\text{Zn dust}} \underset{\substack{\text{2-Ethyl-} \\ \text{pyridine}}}{C_7H_9N}$$

Tropine iodide is formed by the replacement of the alcoholic group in tropine by an iodine atom which on reduction is replaced by hydrogen atom to give dihydrotropidine (tropane). On distillation of its hydrochloride it loses CH_3Cl showing the presence of an *N*-methyl group. Formation of 2-ethylpyridine on distillation with zinc dust suggests the presence of pyridine nucleus in reduced form in tropine.

(*iv*) Based on these experimental observations, Ladenburg suggested the following alternative structures for tropine :



OR

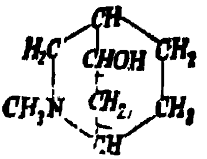


(*v*) Merling (1891) obtained (±) tropinic acid by the oxidation of tropine with chromic anhydride.

$$\underset{\text{tropine}}{C_8H_{15}ON} \xrightarrow{CrO_3} \underset{(\pm)\ \text{tropinic acid}}{C_8H_{13}O_4N}$$

Tropinic acid is a dicarboxylic acid and oxidation of tropine to tropinic acid takes place without the elimination of any carbon atom. This suggests that the hydroxyl group in tropine must be present in a ring system. Ladenburg formula is, therefore, untenable.

(*vi*) Merling proposed the following structures for tropine, both having the hydroxyl group in a ring system.



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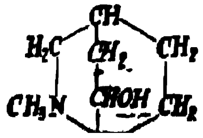

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* *nor* indicates absence of methyl group.

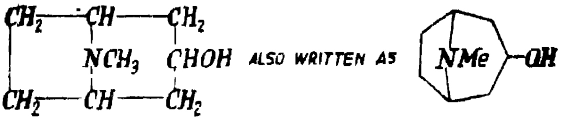
(*vii*) Willstatter (1895—1901) studied the products obtained on oxidation of tropine with chromic anhydride.

$$\underset{\text{Tropine}}{C_8H_{15}ON} \xrightarrow{CrO_3} \underset{\text{Tropinone}}{C_8H_{13}ON} \xrightarrow{CrO_3} \underset{(\pm)\text{-Tropinic acid}}{C_8H_{13}O_4N}$$

Since tropinone behaved as a ketone, tropine must be a secondary alcohol which gives the ketone on oxidation.

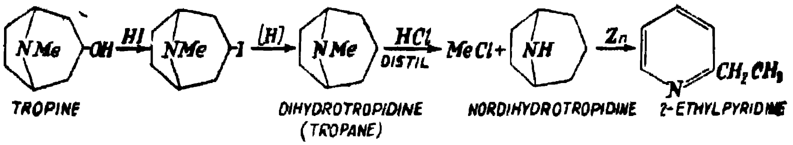
He also showed that tropinone forms a dibenzylidene derivative with benzaldehyde and a di-oximino derivative when treated with amyl nitrite and hydrochloric acid. This suggests the presence of $-CH_2.CO.CH_2-$ grouping in tropinone. No such group is possible in the oxidation product obtained on the basis of Merling formula which is, therefore, untenable.

Willstatter, therefore, proposed three structures for tropine but eliminated two on the consideration of its reactions. He was thus left with only the following formula which contains a pyridine nucleus as well as a pyrrole nucleus with the nitrogen atom common to both.

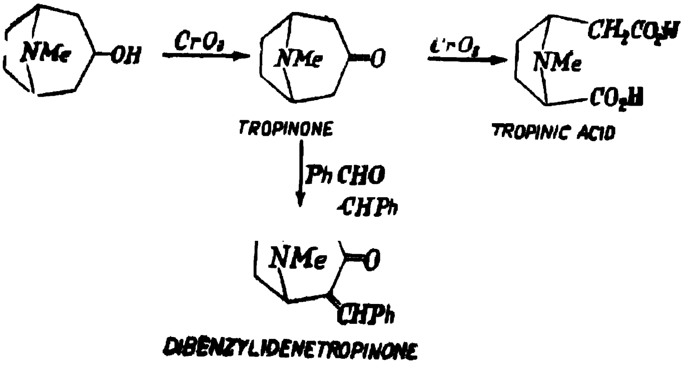


(*viii*) Various reactions of tropine could be readily explained on the basis of this formula. For example,

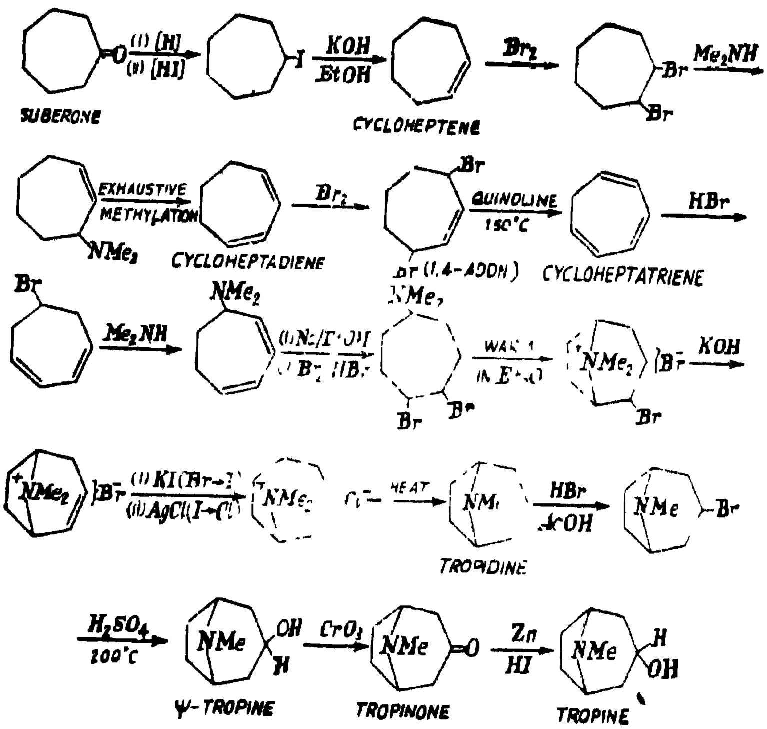
(*a*) *Formation of 2-ethylpyridine from tropine.*



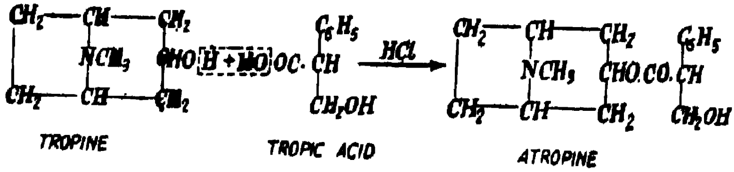
(*b*) *Formation of tropinone, tropinic acid and dibenzylidene tropinone from tropine.*



(ix) The formula assigned to tropine has been finally confirmed by its synthesis (*Willstatter synthesis*).



(6) **Constitution of Atropine.** Atropine being the tropine ester of tropic acid can be obtained by heating their mixture in the presence of hydrogen chloride and can be formulated as under :



*10. **Quinine, $C_{20}H_{24}O_2N_2$.**—Quinine and cinchonine are two most important alkaloids present in the bark of the cinchona tree (*cinchona officinalis*) originally found only in South America. At present it is grown in other tropical countries also like India, Sri Lanka and Java. But Java is the main cultivator of cinchona and has a somewhat monopoly in the production of quinine.

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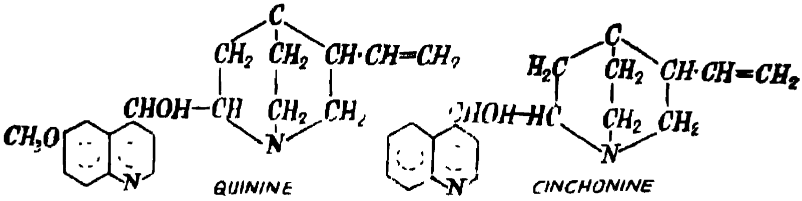
*Alkaloids Quinine, Cinchonine and Morphine have been just mentioned with their formulae to satisfy curiosity of our readers. These are not included in the syllabus for B.Sc. students in any university.

For extraction cinchona bark is powdered and treated with alkali until it gives a semi-solid mass. This is allowed to stand overnight and the alkaloids present are extracted with hot petroleum ether. The extract is treated with dilute sulphuric acid when the alkaloids pass in solution formimg sulphates. The acid solution is partially neutralized and concentrated when quinine sulphate being comparatively less soluble crystallizes out. This is separated and recrystallized.

Properties. Quinine is a white solid (m.p. 450K) with a bitter taste. It is almost insoluble in water but soluble in organic solvents. It is optically active and the natural product is *laevorotatory*, $[\alpha]_D = -158 \cdot 2°$. It is antipyretic and is used in lowering body temperature. It kills the micro-organisms that cause malaria and its salts (sulphate and chloride) were used as specific for the treatment of malaria

Structurally quinine is made up of two heterocyclic units—quinoline and quinuclidine joined through a hydroxymethylene (—CHOH—) group as shown below :



QUININE

CINCHONINE

11. **Cinchonine**, $C_{19}H_{22}ON$.—It is a white optically active solid (m.p. 537K) $[\alpha]_D = +234°$. Its structure is similar to that of quinine except that the methoxy group is absent as shown above.

12. **Morphine**, $C_{17}H_{19}O_3N$.—Morphine (m.p. 527K) is the chief alkaloid present in opium obtained from poppy (*Papaver somniferum*).

Morphine hydrochloride is commonly used in medicine as a soporific and for the alleviation of pain

QUESTIONS

Essay Type :

1 Define an alkaloid and outline methods for the extraction of alkaloids from plant materials. What are their uses ? (*Delhi B.Sc 1978*)

2. Write an explanatory note on : 'General characteristics of alkaloids' (*Delhi B.Sc. 1978*)

3. Describe the preparation, synthesis and properties of coniine Establish its constitution. (*Madras B.Sc. 1971 ; Delhi 1978*)

4 What do you understand by the term alkaloid ? Give an account of isolation of nicotine and the evidence in favour of the structure assigned to nicotine. (*Bangalore B.Sc. 1974 ; Madras 1974, 73*)

5. Write what you know about the preparation, properties and synthesis of piperine. Discuss its structure.

6. Discuss the constitution of alcohol obtained by the hydrolysis of atropine. *(Delhi B.Sc. Hons. 1972)*

(*b*) Describe one synthesis of nicotine.

(Delhi B.Sc. Hons. 1979, 76, 73)

7. How was the structure of nicotine established ?

(Delhi B.Sc. Hons. 1974)

8. (*a*) How is tropic acid obtained from atropine ? Give evidence for the structure of tropic acid. *(Delhi B.Sc. Hons. 1980, 74)*

9. Discuss the structure of atropine. *(Mysore B. Sc. 1972)*

Short Answer Type :

1. What are alkaloid reagents ? *(Mysore B.Sc. 1972)*

2. How would you show that—

Pyrrolidine and pyridine nuclei are joined in nicotine at α-position in the former and β-position in the latter. *(Delhi B.Sc. Hons. 1976, 73)*

3. (*a*) How would you show that—

(*i*) Nicotine contains a pyrrolidine nucleus ? *(Delhi B.Sc. Hons. 1976)*

4. Give the synthesis of tropinone. *(Delhi B.Sc. Hons. 1975)*

5. In a Zeisel's determination for methoxy groups one gram of a substance of the formula $C_8H_8O_3$ gave after treatment with red phosphorus, iodine and water, and the decomposition of the resulting methyl iodide with alcoholic $AgNO_3$, 2·67 g of AgI. Calculate how many methoxy groups are present in the molecule.

[**Ans.** one]

6. Exhaustive methylation has been an important tool in the study of the structure of alkaloids. Illustrate the statement by giving examples of two alkaloids you have studied.

7. What is piperidine ? How are piperidine and coniine related to each other ? *(Delhi B.Sc. 1977)*

8. (*a*) What are alkaloids ?

(*b*) How is nicotine isolated from tobacco leaves ?

(*c*) How will you establish the structure of tropine and tropic acid ?

(Delhi B.Sc. Hons. 1979)

9. How would you establish the linkage between pyridine and pyrollidine nuclei present in nicotine ? *(Delhi B.Sc. Hons. 1978)*

10. (*a*) Outline steps in the synthesis of tropine by Willstatter's method.

(*b*) How is heterocyclic system identified in an alkaloid by Hofmann exhaustive methylation method ? *(Delhi B Sc. Hons. 1979)*

9

Terpenoids

1. Introduction.—The terpenoids constitute a group of compounds majority of which are highly widespread in the plant kingdom. A few of them have also been obtained from other sources. Terpenoid hydrocarbons with few exceptions have the molecular formula $(C_5H_8)_n$ and the value of *n* has been used as a basis for the classification of terpenoids.

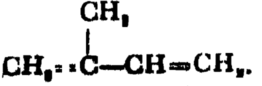
	Value of n	*Formula*	*Class*
(*i*)	2	$C_{10}H_{16}$	Monoterpenoids
(*ii*)	3	$C_{15}H_{24}$	Sesquiterpenoids
(*iii*)	4	$C_{20}H_{32}$	Diterpenoids
(*iv*)	5	$C_{25}H_{40}$	Sesterterpenoids
(*v*)	6	$C_{30}H_{18}$	Triterpenoids
(*vi*)	8	$C_{40}H_{64}$	Tetraterpenoids (Carotenoids)
(*vii*)	>8	$(C_5H_8)_n$	Polyterpenoids

In addition to these terpenoid hydrocarbons, there are oxygenated derivatives of each class. These are mainly alcohols, aldehydes or ketones.

Terpenoids were previously termed terpenes and this name is still being used. The suffix 'ene' is used for unsaturated hydrocarbons. The name 'terpene' is, therefore, inappropriate for the group which includes compounds such as alcohols, aldehydes, ketones, etc. There is a tendency, therefore, to use the more general term 'terpenoids'. The term 'terpene' is at present rather restricted to the hydrocarbon, $C_{10}H_{16}$.

The simpler mono- and sesqui-terpenoids and the related oxygen-containing substances are highly widespread in the plant kingdom. Volatile oils contained in different parts of the plants (roots, stem, leaves, flowers and fruits) are separated by steam distillation These are called *essential* oils and have a strong and pleasant odour. These oils are responsible for the odours and flavours associated with plants. Due to their pleasant odour, essential oils have been used as perfumes since long. Essential oils are mixtures of terpenoid hydrocarbons and their oxygenated derivatives. Some essential oils, *e.g.*, lemon, orange and turpentine oil, are almost exclusive mixtures of terpenoids.

2. Isoprene Rule.—Terpenoids, with few exceptions, have the empirical formula C_5H_8. Their structural formulae suggest that terpenoids are polymers of isoprene.

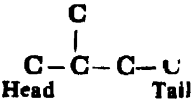


$$CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}CH{=}CH_2.$$

On this account they are sometimes referred to as ***isoprenoid compounds***.

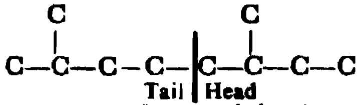
Products of thermal decomposition of terpenoids invariably contain isoprene as one of the constituents. This led Wallach (1887) to suggest *that the skeleton structures of all naturally occurring terpenoids are built up of isoprene units*. This is known as the **isoprene rule**.

According to Ingold (1925), molecules of terpenoids are built of isoprene units joined head to tail. The branched end of the isoprene molecule is termed the *head* and the other end is called the *tail*.



$C-\overset{C}{\overset{|}{C}}-C-C$

(*Isoprene skeleton*)



$C-\overset{C}{\overset{|}{C}}-C-C\,|\,C-\overset{C}{\overset{|}{C}}-C-C$

(*Myrcene skeleton*)

This divisibility of terpenoids into isoprene units and their head to tail union is referred to as **Ingold's special isoprene rule.** This rule can, however, be used only as a guiding principle and not as a fixed rule since there are several exceptions to the rule.

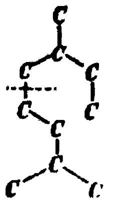
Monoterpenoid molecule ($C_{10}H_{16}$) contains six hydrogen atoms less than the molecule of corresponding alkane ($C_{10}H_{22}$). Since each double bond or ring reduces the number of hydrogen atoms by two, shortage of six hydrogen atoms can be accounted for in three different ways giving rise to three different groups of monoterpenoids given below :

(*i*) *Open-chain or Acyclic monoterpenoids* containing three double bonds.

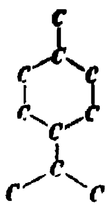
(*ii*) *Monocyclic monoterpenoids* containing one carbon ring and two double bonds.

(*iii*) *Bicyclic monoterpenoids* containing two carbon rings and one double bond.

Monocyclic monoterpenoids contain a six-membered ring. Ingold pointed out that the presence of a gem-dialkyl group renders the cyclohexane ring more stable. This *gem-dialkyl rule*, stated by Ingold, limits the number of possible structures obtained by closing the open chain to a cyclohexane ring. Thus the monoterpenoid open chain can give rise to only one monocyclic monoterpenoid, *viz.*, the *p*-cymene structure. Most of the naturally occurring monocyclic monoterpenoids are derivatives of *p*-cymene.



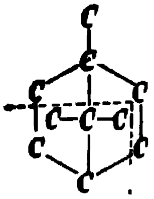
acyclic structure

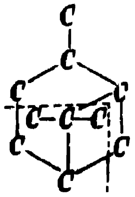


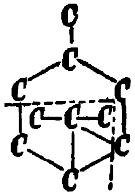
p-cymene structure

The acyclic structure is also written above in the conventional ring shape'.

Bicyclic monoterpenoids contain a six-member ring along with another three-, four- or five-member ring. Presence of a *gem*-dimethyl group in these cyclopropane and cyclobutane rings is essential to render them sufficiently stable for occurrence in nature. Three possible skeletons of a bicyclic monoterpenoid are :







Bicyclic monoterpenoids with all the three types of skeletons are known.

3. Isolation and General Properties of Terpenoids. Essential oils are extracted from plants mainly by steam distillation. Plant tissues (roots, stem, leaves, flowers or fruits) are macerated and steam-distilled when the essential oils distil over. In case constituents of the essential oil decompose on steam distillation, it is extracted with a solvent, *e.g.*, light petrol at 320K. From the solution so obtained, the solvent is distilled away at reduced pressure. Still another method which may be employed is adsorption in fats. For example, to extract the essential oil present in flower petals these are spread over purified molten fat until the latter is saturated with the essential oil which may be extracted from the resultant fat with ethanol. Terpenoids are obtained from the essential oil by fractional distillation.

As far as physical properties are concerned, majority of the terpenoids are colourless liquids which are lighter than water and boil between 410K and 460K. A few of them are solids. These are lighter than water, volatile in steam, usually highly refractive and insoluble in water but soluble in organic solvents. Most of these are optically active.

Chemically these are unsaturated compounds (open-chain or cyclic with one or more carbon atom rings) containing one or more double bonds. Consequently terpenoids give addition products with hydrogen, halogens, halogen acids. Some of them form crystalline hydrates. They undergo polymerisation, oxidation and also dehydrogenation in the ring. With NO_2, NOCl and NOBr, terpenoids give characteristic addition products which are useful in their identification. A number of them possess antiseptic properties.

ACYCLIC MONOTERPENOIDS

4. Myrcene, $C_{10}H_{16}$.—This is an acyclic monoterpenoid hydrocarbon (*i.e.*, a terpene). It is a colourless oil (b.p. 439-441K) which occurs in verbena and bay oils. It gives reactions of a triolefin.

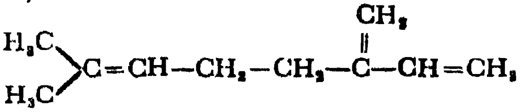
Constitution. (*i*) Molecular formula of myrcene, as deduced from its analytical data, is $C_{10}H_{16}$.

(*ii*) Myrcene on catalytic hydrogenation in the presence of platinum gives decane, $C_{10}H_{22}$. This shows that it is *an open-chain compound containing three double bonds.*

(*iii*) It forms an addition compound with maleic anhydride (Diels-Alder reaction). This indicates the *presence of two conjugated double bonds in myrcene.* This is further supported by the fact that myrcene shows optical exaltation.

(*iv*) Ozonolysis of myrcene produces acetone, formaldehyde and a ketoaldehyde, $C_5H_8O_2$, which on oxidation with chromic acid gives succinic acid and carbon dioxide.

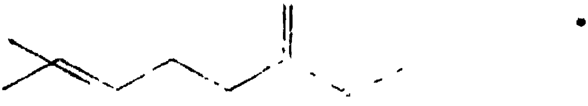
(*v*) These results can be explained by assigning the following structure to myrcene :



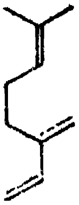
$$\begin{matrix} H_3C \\ H_3C \end{matrix}\!\!>C=CH-CH_2-CH_2-\overset{\overset{\displaystyle CH_2}{\|}}{C}-CH=CH_2$$

Thus myrcene is 7-methyl-3-methylene-1, 6-octadiene.

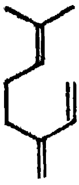
In terpenoid chemistry it has been customary to use conventional formulae wherein only lines are used. Carbon atoms are situated at the junction of pairs of lines and at the ends. Double bonds are indicated by double lines. Thus myrcene could be represented by the following skeleton drawn in a zig-zag fashion.



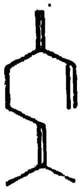
It is, however, a common practice in terpenoid chemistry to draw these skeletons in the form of a ring (an open cyclohexane ring) Thus myrcene could be given any one of the following three conventional formulae



I



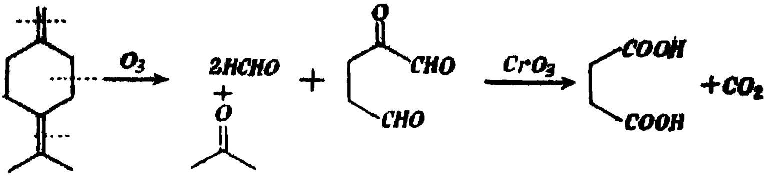
II



III

Out of these III is the one that is now recommended for use.

The products of ozonolysis and oxidation of ketoaldehyde can be represented as follows :



Myrecene **Acetone** **Ketoaldehyde ($C_5H_6O_3$)** **Succinic acid**

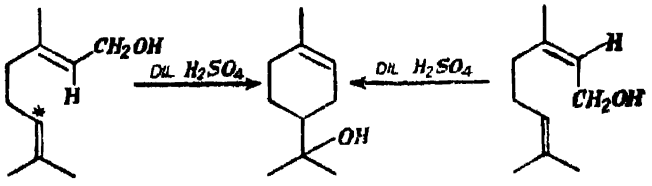
(*vi*) This structure is supported by the fact that myrcene on hydration in presence of dilute sulphuric acid gives an alcohol which on oxidation gives citral Structure of citral is known and is in accord with this assigned structure of myrcene.

5. **Geraniol, $C_{10}H_{18}O$.**—Geraniol occurs in rose, lemon-grass, geranium, lavender and citronella oils. It is obtained from the cheap oil of palmrosa by treating with anhydrous calcium chloride and decomposing the crystalline addition product thus obtained with water. It may also be obtained by reduction of citral (corresponding aldehyde) with aluminium amalgam, but some **nerol** is also formed at the same time. Structural identity of geraniol and nerol is shown by the following facts :

(*i*) On catalytic hydrogenation both add two molecules of hydrogen and give the same saturated alcohol, $C_{10}H_{22}O$.

(*ii*) On oxidation, both give the same oxidation products which give the position of double bonds also as 2 and 7.

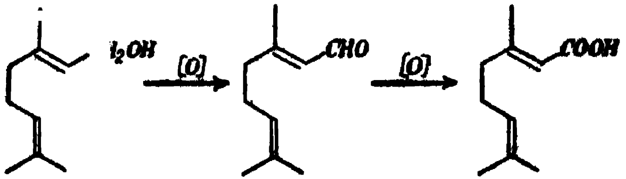
Hence geraniol and nerol are geometrical isomers. Cyclisation of nerol to α-terpineol by means of dilute sulphuric acid takes place about 9 times as fast as the cyclisation of geraniol. Based on this observation nerol has been assigned *cis* configuration whereas geraniol has been assigned *trans* configuration. Faster rate of cyclisation with nerol is due to the proximity of the alcoholic group to the carbon (*) which is involved in the ring formation.



Geraniol (*Trans*) α-Terpineol Nerol (*Cis*)

Nerol is found in neroli oil, cyclamen oil and bergamot oil and is obtained from them.

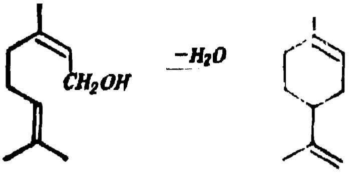
Properties. Both geraniol and nerol are colourless liquids having pleasant rose-like odour. Due to the presence of two double bonds and a primary alcoholic group they exhibit the reactions of a diolefin and a primary alcohol (*i*) On oxidation geraniol gives citral which on further oxidation gives geranic acid.



Geraniol Citral Geranic acid

(*ii*) Both geraniol and nerol react with dilute sulphuric acid to give a cyclic terpene—α-terpineol. This may be viewed as taking place by loss of a molecule of water resulting in ring closure followed by hydration of the side chain at the position of double bond.

(*iii*) Nerol readily loses water to form dipentene (a cyclic hydrocarbon).



Nerol Dipentene or Limonene

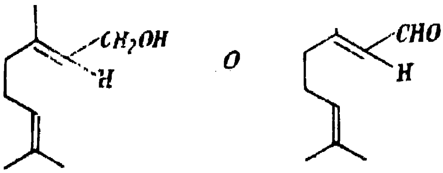
Constitution of Geraniol. (*i*) Molecular formula of geraniol as deduced from its analytical data is $C_{10}H_{18}O$.

(*ii*) It gives the reactions of a diolefin, *e.g.*, on bromination it gives a tetrabromide and four hydrogen atoms are added during reduction. This shows the presence of two double bonds.

(*iii*) It exhibits the reactions of a primary alcohol, *e.g.*, on oxidation it gives an aldehyde (citral-*a*) and on further oxidation gives an acid (geranic acid) containing the same number of carbon atoms.

(*iv*) Arrangement of carbon atoms in its molecule is the same as in citral which it gives on oxidation. For structure of citral *see* page 2·856.

(*v*) Hence structural formula of geraniol is :



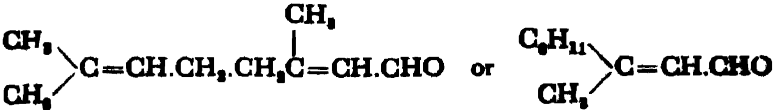
Geraniol Citral-*a*

(*vi*) This explains the formation of α-terpineol by ring closure.

6. Citral, $C_{10}H_{16}O$.—This is the most important acyclic terpenoid since the structures of most of the other monoterpenoids are based on the structure of citral. It occurs in oil of lemon-grass (70-80%) and oils of lime, lemon, citronella, etc.

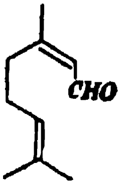
Extraction. It is obtained from lemon-grass oil by fractional distillation under reduced pressure and purified by forming the bisulphite compound. The crystalline bisulphite compound is decomposed with sodium carbonate to get free citral.

Properties. Citral is a pale yellow oily liquid (b.p. 497-501K) with a pleasant odour of lemons. Chemical formula of citral is

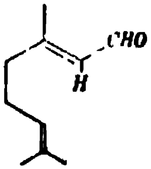


$$\begin{array}{l}CH_3\\ \quad\rangle C{=}CH.CH_2.CH_2\overset{\overset{\large CH_3}{|}}{C}{=}CH.CHO\\ CH_3\end{array} \quad \text{or} \quad \begin{array}{l}C_6H_{11}\\ \quad\rangle C{=}CH.CHO\\ CH_3\end{array}$$

and its conventional formula is given below. The formula shows



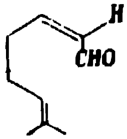
that it can exhibit geometric isomerism. Two isomers of citral are :



OR

$$\begin{array}{c}C_6H_{11}-C-CH_3\\ \|\\ H-C-CHO\end{array} \quad \text{AND} \quad \begin{array}{c}C_6H_{11}-C-CH_3\\ \|\\ OHC-C-H\end{array}$$

OR



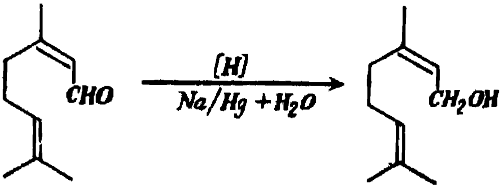
trans- (or E-) form
Citral-*a* (*geranial*)
b.p. 391-392K/20 mm.

cis-(or Z-) form
Citral-*b* (*neral*)
b.p. 390-391K/20 mm

Citral-*a* or geranial is given when geraniol is oxidised whereas citral-*b* or neral is produced when nerol is oxidised. Commercial citral is a mixture of citral-*a* (20%) and citral-*b* (10%).

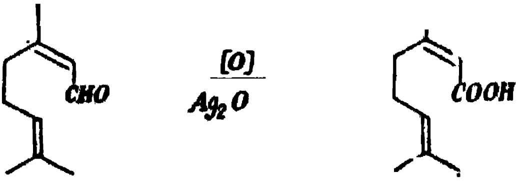
Some chemical reactions of citral are :

(*i*) **Reduction.** Citral on reduction with sodium amalgam and water gives geraniol.



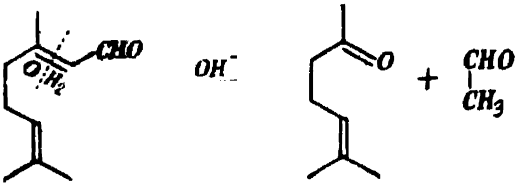
Citral Geraniol

(*ii*) **Oxidation**. On oxidation with silver oxide, it gives geranic acid.



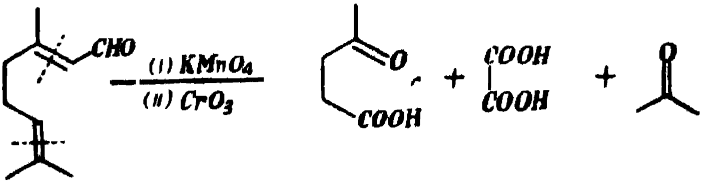
Geranic acid

(*iii*) **Hydrolysis.** When heated with potassium carbonate solution, citral undergoes hydrolysis and yields 6-methyl-5-hepten-2-one and acetaldehyde. During this reaction citral undergoes cleavage at the α, β-double bond. This cleavage by alkaline reagents is a general reaction of α, β- unsaturated oxo-compounds.



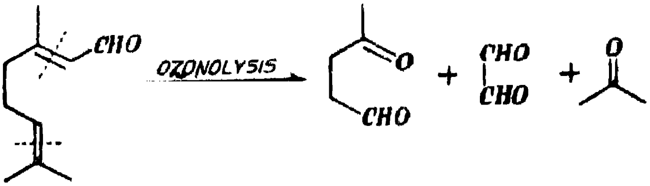
Citral 6-Methyl-5-hepten-2-one

(*iv*) **Oxidation with alk. KMnO$_4$** followed by chromic acid gives acetone, oxalic acid and laevulic acid.



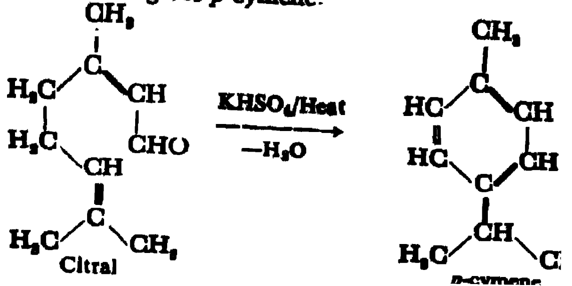
Citral Laevulic acid Acetone

(*v*) **Ozonolysis.** On ozonolysis it gives acetone, laevulaldehyde and glyoxal.



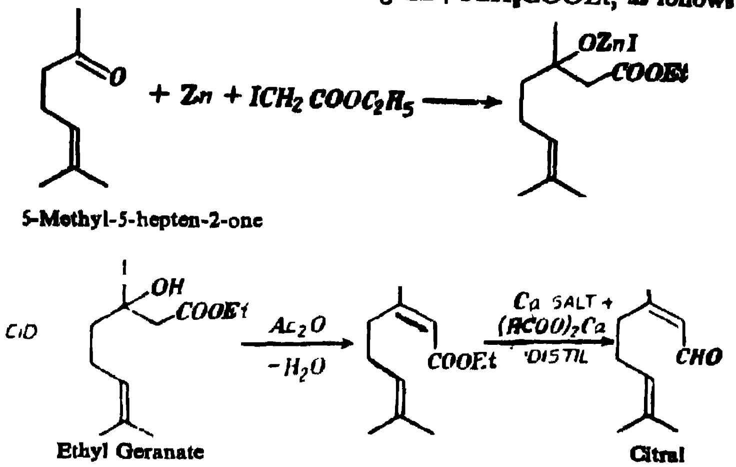
Citral Laevulaldehyde Glyoxal Acetone

(*vi*) **Dehydration.** On heating with $KHSO_4$, citral loses a molecule of water and gives *p*-cymene.



These reactions confirm the structure assigned to citral.

Synthesis. Citral may be synthesised from 6-methyl-5-hepten-2-one by Reformatsky reaction using $Zn + ICH_2COOEt$, as follows :



As citral on reduction gives geraniol, these very steps can be used for the synthesis of geraniol.

Uses. It is widely used as flavouring agent and in preparing synthetic perfumes, *e.g*, α- and β-ionone. It is also employed for the manufacture of geraniol.

Constitution of Citral. (*a*) *Molecular formula* of citral as deduced from its analytical data is $C_{10}H_{16}O$.

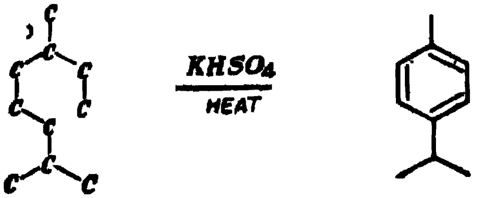
(*b*) *Presence of —CHO group.* It gives the typical reactions of an aldehyde, *e.g.*,

(*i*) It gives bisulphite compound and an oxime.

(*ii*) On oxidation with silver oxide it gives geranic acid, an acid with same number of carbon atoms as citral.

(*c*) *Positions of methyl and isopropyl groups.* On heating with hydrogen sulphate, citral forms *p*-cymene (II), *p*-methyl-

From this Semmler concluded that citral molecule was acyclic and assigned it the structure (I), having two isoprene units joined head to tail.

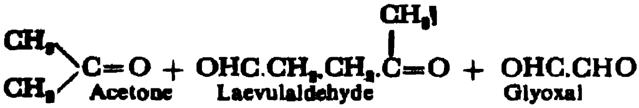


(I)
Proposed skeleton
for citral

(II)
p-cymene
(*p*-methyl-isopropylbenzene)

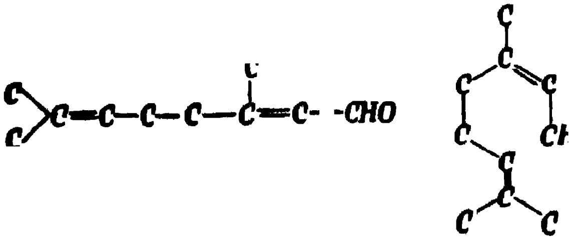
(*d*) *Presence of two double bonds.* On ozonolysis it gives acetone, laevulaldehyde and glyoxal, *i.e.*, the chain breaks at two points. This suggests the presence of two double bonds.

(*e*) *Location of two double bonds.* The carbon atoms in the molecule are arranged as in the above three products and with—CHO at one end.

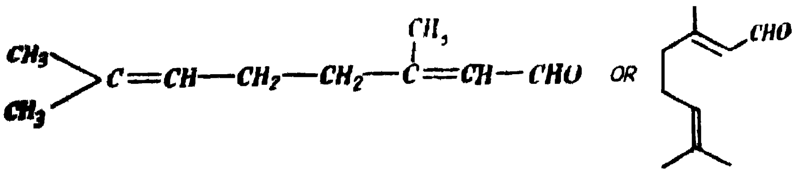


$$\underset{\text{Acetone}}{(CH_3)_2C{=}O} + \underset{\text{Laevulaldehyde}}{OHC.CH_2.CH_2.\overset{CH_3}{\overset{|}{C}}{=}O} + \underset{\text{Glyoxal}}{OHC.CHO}$$

Hence the skeleton is



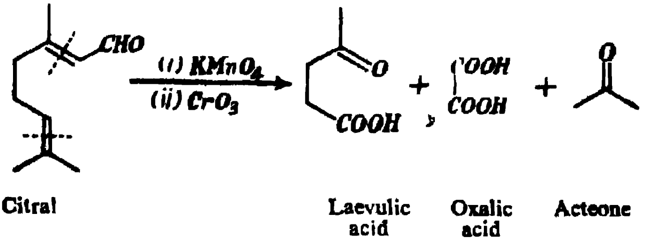
(*f*) *Structural formula.* From this we can write the structural formula of citral as



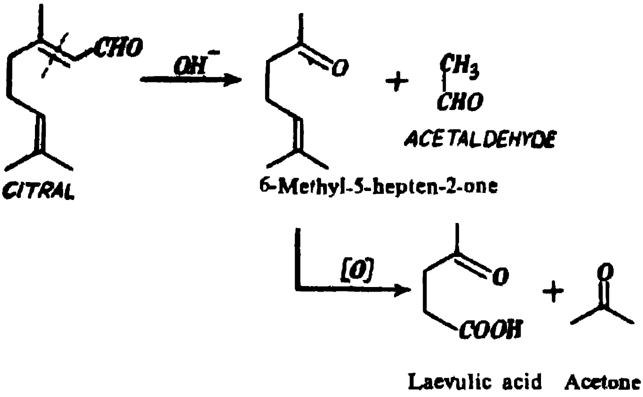
$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C{=}CH{-}CH_2{-}CH_2{-}\overset{CH_3}{\overset{|}{C}}{=}CH{-}CHO \quad \text{OR}$$

(*g*) *Further support.* The structural formula assigned to citral as given above is supported by the following two reactions of citral :

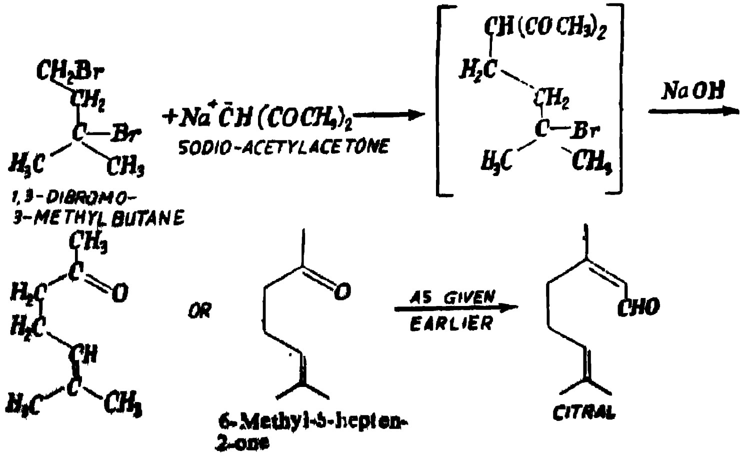
(*i*) *Oxidation.* Oxidation of citral with alkaline permanganate, followed by chromic acid, gives acetone, oxalic acid and laevulic acid. Formation of these oxidation products is in accordance with the assigned structural formula of citral.



(*ii*) *Hydrolysis*. Structure assigned to citral is further supported by its hydrolysis with aqueous potassium carbonate. Products of hydrolysis are acetaldehyde and 6-methyl-5-hepten-2-one which itself on oxidation gives acetone and laevulic acid. This is in accord with the assigned structural formula of citral.



(*h*) *Final confirmation*. The structure of citral was finally confirmed by the synthesis of methylheptenone given below and its conversion into citral as given on page 3·181.

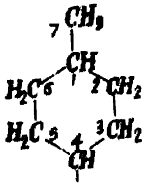


MONOCYCLIC MONOTERPENOIDS

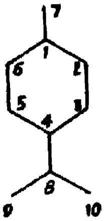
7. **Nomenclature.**—For purposes of nomenclature of the monocyclic monoterpenoids *p*-menthane (*p*-methylisopropyl cyclohexane or hexahydro-*p*-cyamene), $C_{10}H_{20}$ is used as the parent hydrocarbon.

(I) is the structural formula of *p*-menthane whereas (II) is the conventional method for drawing the same.

Various carbon atoms in *p*-menthane are numbered as given below and the positions of substituents and double bonds in its derivatives are indicated by numbers.

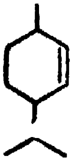


OR

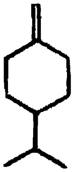


(I) (II)

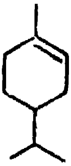
When a derivative of *p*-menthane contains one or more double [illegible]s, sometimes ambiguity may arise regarding the exact position of the double bond. To prevent it, in addition to a number which locates the first carbon joined to the double bond, the second carbon atom joined to the double bond is also shown, but it is placed in parentheses. For example,



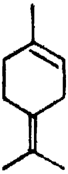
2-*p*-Menthene
(1)



1(7)*p*-Menthene
(2)



1(2)-*p*-menthene
(3)



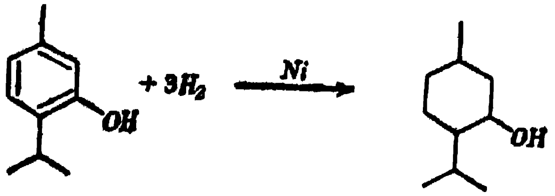
1, 4 (8)
p-Menthadiene
(4)

There could be no ambiguity regarding the position of double bond in 2-*p*-menthene [Formula (1)], so the second carbon atom joined to the double bond need not be given.

In (2), (3) and (4) such ambiguity is possible hence showing of second carbon atom joined to the double bond in each case is essential.

8. **Menthol, (3-*p*-menthanol) $C_{10}H_{19}OH$.**—Menthane is a synthetic compound (b.p. 443K). It does not occur in nature but its alcohol (menthol) is the chief constituent of oil of peppermint.

Preparation. (*i*) Menthol, being the chief constituent of oil of peppermint, is prepared from it by crystallization on simple cooling. Crystals are separated by pressing and purified by recr (*ii*) It is also prepared by catalytic hydrogenation of thymol.

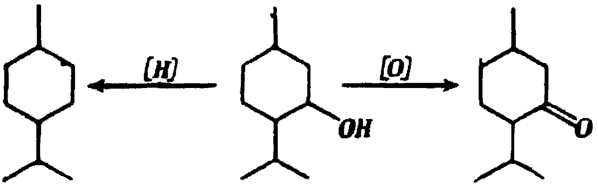


Thymol Menthol

Properties. Menthol forms colourless, volatile prismatic crystals (m.p. 318K and b.p. 485K) having strong peppermint odour and a cooling taste. It is optically active due to the presence of three asymmetric carbon atoms (1, 3 and 4) and exists in 8 isomeric forms. Naturally-occurring isomer is (–)-menthol. Synthetic menthol is a (±)-mixture.

Chemically it behaves as an alicyclic secondary alcohol as illustrated by its reactions given below :

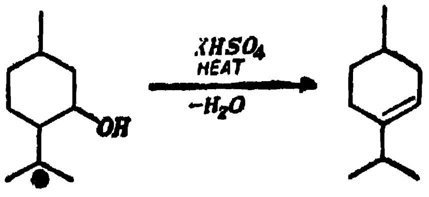
(*i*) **Oxidation.** It is oxidised by chromic acid-sulphuric acid mixture to give menthone, the corresponding ketone (*property of secondary alcohol*).



Menthane Menthol Menthone

(*ii*) **Reduction.** It gives menthane when reduced with hydriodic acid as shown above.

(*iii*) **Dehydration.** Menthol loses a molecule of water when heated with potassium hydrogen sulphate and yields 3-Menthene.



Menthol 3-Menthene

Uses. (*i*) As an antiseptic in ointments, nasal sprays and gargles.

(*ii*) Due to the cooling effect it produces on the skin, it relieves headache.

(*iii*) In medicine and pharmaceuticals.

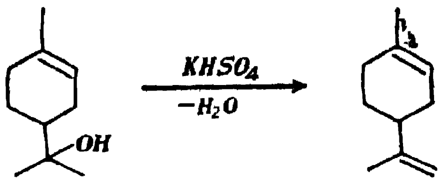
(*iv*) In perfume industry (for tooth-pastes and tooth-powders).

9. Limonene, *1, 8 (9)*-Menthadiene, $C_{10}H_{16}$

Limonene is a very widely-distributed terpenoid. It has an asymmetric carbon atom (shown by C) and is, therefore, optically active. (+)-Limonene is the principal terpene in lemon, orange, bergamot, caraway and celery oils. (—)-Limonene is obtained from the needles of the Douglas fir. The inactive (±)-mixture, called **dipentene**, occurs in lemon-grass oil and turpentine oil.

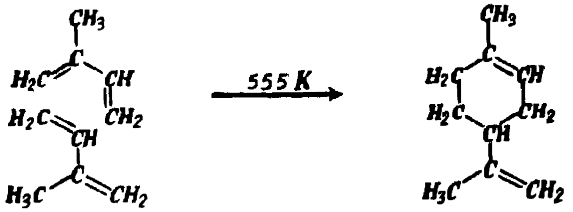
Preparation. (*i*) *From Essential Oils.* (+)-Limonene is obtained from orange. Dipentene is extracted from terpentine oil

(*ii*) *By dehydration of α-terpineol with* $KHSO_4$.



α-Terpineol Limonene

(*iii*) *By heating isoprene to* 555K (*Diels-Alder 1 : 4-addition reaction*).

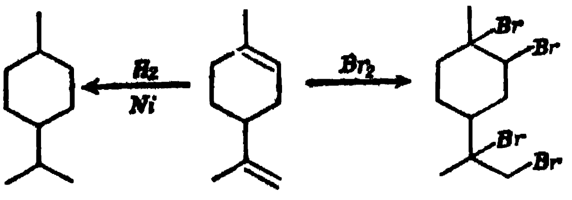


Isoprene
(2 molecules)

Limonene

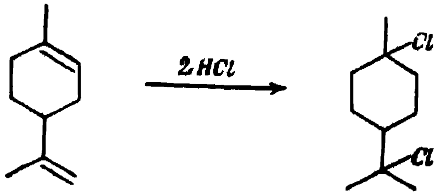
Properties. Limonene is a pleasant-smelling liquid with citrus-like odour (b.p. 450K). It is insoluble in water. Chemically it gives the reactions of a diolefin. For example,

(*i*) It forms addition products with hydrogen to give *p*-menthane and bromine to give crystalline tetrabromide.



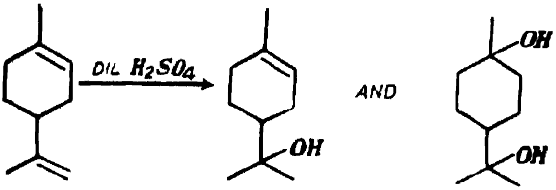
p Menthane Limonene Limonene tetrabromide

(*ii*) It gives an addition product with two molecules of halogen acids.



Limonene Addition product

(*iii*) With dilute sulphuric acid it gives α-terpineol and terpin hydrate *



Limonene α-Terpineol Terpin

(*iv*) *With concentrated sulphuric acid it polymerizes*

Uses. (*i*) *(+)-Limonene is used as flavouring agent in beverages and foods.*

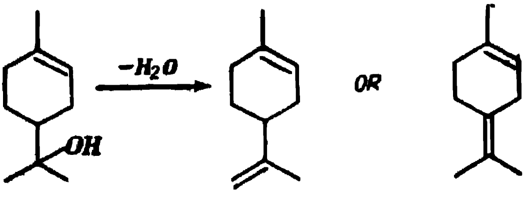
(*ii*) Dipentene is used in medicine and in making synthetic resins and high pressure lubricating oil additives. It is also used in the synthesis of isoprene, *p*-cymene and *p*-menthane

Constitution of Limonene (*i*) *Molecular formula of limonene*, deduced from its analytical data, is $C_{10}H_{16}$.

(*ii*) *Presence of two double bonds* in it is indicated by the additionof 4 bromine atoms to give the tetrabromide.

(*iii*) *Structure of carbon framework* is the same as in *menthane* which it gives on catalytic hydrogenation.

(*iv*) *Position of the two double bonds* in the above framework follows from its formation when α-terpineol (1-menthene-8-ol)is heated with $KHSO_4$ and its conversion to α-terpineol by shaking with dil. H_2SO_4. One double bond was already present in α-terpineol between carbon atoms 1 and 2 and another came into existence due to loss of water between carbon atoms 8 and 9 or between carbon atoms 4 and 8



α-Terpineol (I) (II)

---

* Terpin (*a liquid*) is $C_{10}H_{18}(OH)_2$ and terpin hydrate (*crystalline compound*) is $C_{10}H_{18}(OH)_2.H_2O$ which gives up the molecule of water of crystallization readily.

Thus carbon skeleton and position of one double bond are known. Position of the second double bond is uncertain and it might have structure I or II.

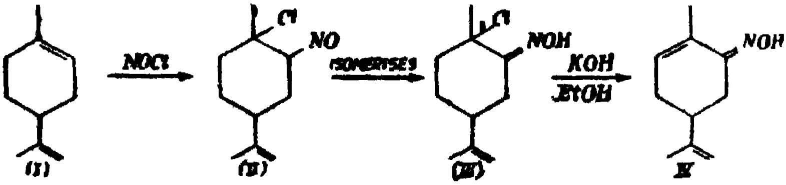
(v) *Proof of position 8 (9).*

(a) Structure I contains one chiral carbon atom (C_4) and hence exhibits optical activity. Structure II is symmetrical and cannot, therefore, be optically active. Limonene being optically active, formula II is ruled out. Hence formula I must be the structural formula of limonene.

(b) *Chemical Proof for position 8(9).* Chemical proof for position 8(9) is afforded by the following reactions :

$$\underset{(I)}{\text{Limonene}} \xrightarrow{\text{NOCl}} \underset{(III)}{\text{Limonene nitrosochloride}} \xrightarrow[\text{EtOH}]{\text{KOH}} \underset{(IV)}{\text{Carvoxime}}$$

Structure of carvoxime is known and it has a double bond in position 8(9). It, therefore, follows that limonene must have the structure I with double bond in position 8(9). Thus the above reaction may be written as follows :



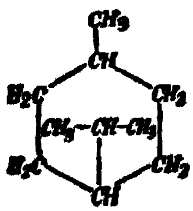
(vi) Hence limonene is 1, 8(9)-menthadiene, structure (I) given above.

BICYCLIC MONOTERPENOIDS

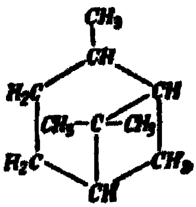
10. **Introduction.**—The bicyclic monoterpenoids are hydrocarbons containing two rings and one double bond and their derivatives. One of the rings is always a six-member ring while second ring may be a 3-, 4- or 5-member ring. Thus there are three classes of bicyclic terpenoids according to the size of the second ring.

11. **α-Pinene** $C_{10}H_{16}$. It makes the bulk of turpentine oil and is the most widely distributed of all natural terpenoids. It is also found in eucalyptus oil.

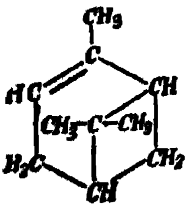
(i) It is an optically active liquid (b.p. 429K).



Menthane
(*Monocyclic terpenoid*)
[*cf.* formula given on page 3·184]



Pinane
(*Parent hydrocarbon*)



α-Pinene
(*Bicyclic terpenoid*)

(ii) It is readily oxidised. For example, when turpentine oil is added drop by drop to a mixture of fuming nitric acid and concentrated sulphuric acid, swift oxidation produces a flash.

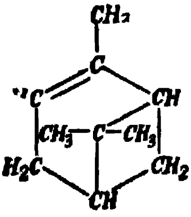
In air it takes a molecule of oxygen forming $C_{10}H_{16}O_2$, a substance of the nature of peroxide which readily supplies an atom of oxygen and hence oxidises other substances. For example, arsenious acid is oxidised to arsenic acid and indigo is decolorised

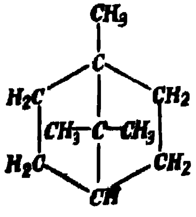
(iii) On passing dry hydrogen chloride through turpentine oil, the product is a compound of pinene and hydrogen chloride, $C_{10}H_{17}Cl$ which resembles camphor in appearance as well as odour, and is on this account wrongly called artificial camphor. Synthetic camphor is, however, a different compound.

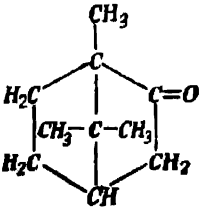
(2) **Turpentine oil.** It is obtained from coniferous trees by removing the bark from a small area of the tree trunk and making an incision in it. The resinous mass that oozes out is called *turpentine*. This is steam-distilled. The distillate obtained is called oil of turpentine and the residue left in the still is called colophony.

Oil of turpentine is used medicinally and in making paints and varnishes.

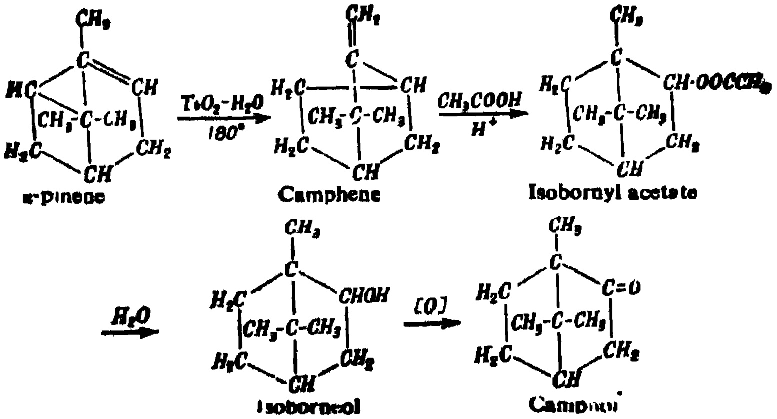
(3) **Camphor, $C_{10}H_{16}O$.** Camphor is prepared by distilling the wood and leaves of camphor laurel with steam. It is related to bicyclic terpene.


α-Pinene
(*Bicyclic terpene*)


Camphane
(*Parent hydrocarbon*)


Camphor

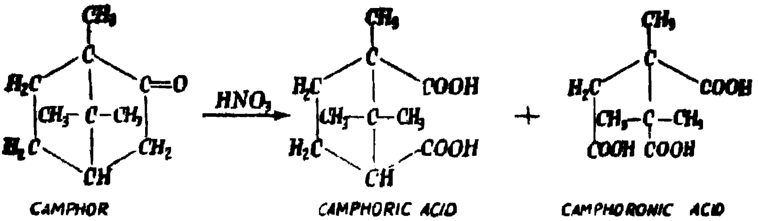
Commercial Preparation of Camphor. Synthetic camphor is obtained from α-pinene as the starting material. Various steps involved in the conversion are given below :



Camphor is a crystalline solid (m.p. 482K ; b.p. 448K) which crystallizes in glistening prisms having a strong characteristic odour. It sublimes at ordinary temperature. Natural camphor is optically active (*dextro-rotatory*) having specific rotation = +44°.

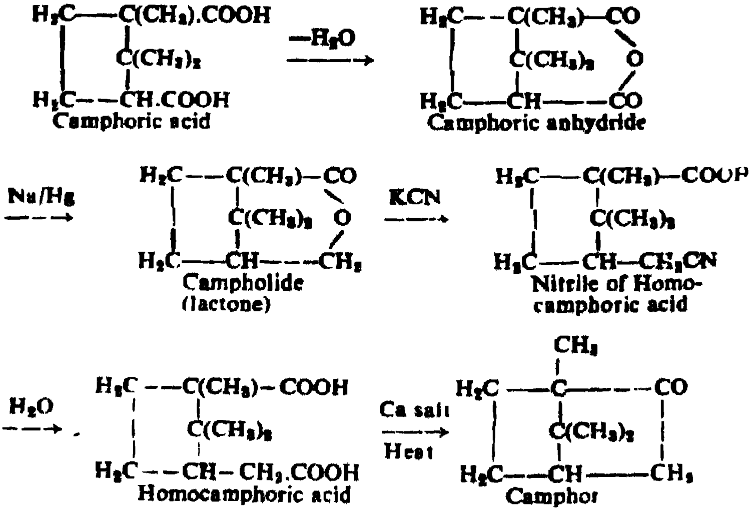
Chemically it shows the properties of a ketone. For example, it forms an oxime and yields a secondary alcohol (*borneol*) on reduction with sodium and alcohol.

Oxidation of camphor with nitric acid gives **camphoric acid**, $C_{10}H_{16}O_4$. Camphoric acid (or camphor) with nitric acid gives **camphoronic acid**, $C_9H_{14}O_6$.



Camphor is used as a moth repellant, as a preservative in cosmetics, in medicine and as a plasticiser in the manufacture of celluloid, smokeless powder, and photographic films.

Synthesis of Camphor from camphoric acid.



QUESTIONS

Essay Type :

1. What are terpenoids ? How are they classified ? How are these extracted ? Write a short note on their chemical nature.

2. (*a*) What are terpenoids ? How are they classified ?

(*b*) How is the structure of citral established ?

(Delhi B.Sc. Hons. 1980, 79, 76, 72)

3. What are the important sources of geraniol ? Discuss its structure. How has it been synthesised ? (Banaras B.Sc. 1972)

4. (a) Describe the preparation, properties and uses of menthol or limonene.

(b) Discuss the constitution of limonene.

5. Discuss the oxidative degradation of camphor. Indicate the products by their structural formulae. Give the synthesis of (i) Camphoronic acid, and (ii) Camphor from camphoric acid. Show how would you convert pinene into camphor.

6. How is the structure of dipentene established ? Write a note on isoprene rule. (Delhi B.Sc. Hons. 1980, 75, 73 ; Mysore B.Sc. 1973)

7. Give one synthesis of methylheptenone. Starting from methylheptenone outline the synthesis of citral using Reformatsky reaction. (Delhi B.Sc. Hons. 1974)

8. (a) Discuss the analytical evidence on the basis of which the structure of alpha-pinene has been established.

(b) How is alpha-pinene converted into camphor ? Mention the important uses of camphor. (Bombay B.Sc. 1974)

Short Answer Type :

1. What do you understand by the term 'terpenoids' ? (Mysore B.Sc. 1972)

2. What are essential oils and why are they so called ? (Delhi B.Sc. Hons. 1973)

3. Give the isolation and uses of any one important essential oil. (Delhi B.Sc. Hons. 1975)

4. How are terpenoids classified ? (Bombay B.Sc. 1972)

5. How do you differentiate between geraniol and nerol ? (Bombay B.Sc. 1972)

6. How will you prove the following :

(i) α-pinene contains a six-member ring.

(ii) Dipentene contains one double bond outside the ring.

(iii) Citral is an unsaturated aldehyde.

(iv) Camphor is a cyclic ketone. (Bombay B.Sc. 1972)

7. Justify with the help of chemical reactions and notes, the validity of the following statements :

(i) Camphor is a bicyclic monoterpenoid.

(ii) α-pinene contains a cyclobutane ring.

(iii) α-terpineol has a tertiary alcoholic group and dipentene has ethylenic bonds in positions 1 and 8. (Bombay B.Sc. 1971)

8. How is 4-keto-hexahydrobenzoic acid converted into dipentene ? (Delhi B.Sc. Hons. 1979)

9. (a) How is citral synthetically obtained from isoprene ?

(b) What happens when—

(i) citral is heated with sodium carbonate ?

(ii) geraniol and nerol are subjected to mild oxidation ? (Delhi B.Sc. Hons. 1978)

10

Biochemistry

1. Living Systems.—The molecules which form the basis of our life are more complex than the organic molecules studied earlier. These are called biomolecules which in turn combine and form the living beings.

Independent performance of functions of life is characteristic of living being. Living creatures need energy to perform these basic functions. Energy is drawn from environments as plants do from sunlight or from raw materials called nutrients. Nutrients consist of water, inorganic mineral salts, complex organic substances called vitamins and basic foods like fats, carbohydrates and proteins. The energy releasing reactions are carried out at body temperature of living organism and at atmospheric pressure, *p*H remaining around 7·0. After extracting energy the processed substances are discarded as waste in various forms from the body. Thus every living system represents a steady state and can adapt itself to the natural environments.

2. Biomolecules—These are complex lifeless organic substances which combine in specific manner to produce life. These are amino acids, fats, carbohydrates, proteins, etc. A living organism may not be able to perform basic functions of life without many simple substances like water, inorganic salts and vitamins. Water may be as high as 20 to 90 per cent body weight. Important biomolecules are discussed in the succeeding paragraphs.

3. **Carbohydrates.**—Glucose, fructose, cane-sugar, starch and cellulose were all considered to be as hydrates of carbon and were, therefore, named as *Carbohydrates*. These have been discussed at length in Chapter 49.

Importance of Carbohydrates for the Living Systems.—Starch and sugars get hydrolysed to glucose by enzymes present in the various juices secreted by different organs in the human and animal digestive systems. Glucose so produced is transported from cell to cell by the blood. Slow combustion of glucose by a series of steps provides energy necessary for functioning of the living body and doing day's work. In plants glucose is carried from cell to cell by sap.

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O + 2{,}832 \text{ kJ}$$

The body stores a part of carbohydrates for the rainy day in liver as glycogen called animal starch. In case of emergency like fasting or illness, glycogen hydrolyses to glucose and thus supplies the necessary energy.

No other food will act so quickly as sugar to supply energy when you feel exhausted. It is speedily digested, assimilated and converted into the requisite fuel.

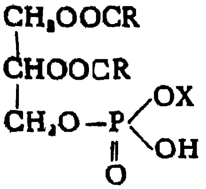
Different enzymes are required for hydrolysis of cellulose. These are absent in the human body but present in the digestive system of various grazing animals which can, therefore, use cellulose of grass and plants as food.

4. **Lipids.**—Fats and oils along with their derivatives occurring in living systems belong to a class of substances called *lipids*. These are sparingly soluble in water but highly soluble in organic solvents.

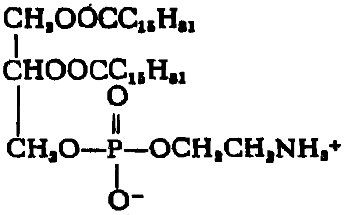
Fats and Oils. Fats and oils are glyceryl esters of different higher fatty acids. Glycerides of unsaturated fatty acids like oleic acid ($C_{17}H_{33}COOH$) are termed unsaturated fats. Similarly glycerides of saturated fatty acids like stearic acid ($C_{17}H_{35}COOH$) and palmitic acid ($C_{15}H_{31}COOH$) are called saturated fats. These are excellent fuels. Fats protect delicate tissues and some of them are important sources of necessary vitamins. Animals fed on fat, free diet over an extended period were found to suffer from skin eruptions. Important sources of fats and oils are meat, dairy products, eggs and nuts. Cottonseed oil and olive oil are wholesome fats.

Place of fats and oils in our diet received a great deal of attention in early sixties because of the possible role of saturated fats in arterial diseases. Fats constitute a concentrated storehouse of energy for animals. For instance, in humans the total carbohydrate stored in the liver as glycogen is just enough to keep the body going for about fifteen hours. Enough fats can, however, be stored in the body to keep it going for months. In contrast to animals, plants store their energy mainly in the form of starch (a carbohydrate). Fats present in the tissues of animals serve as shock-absorbing pads and heat insulators. Fats may also be the components of cell membrane.

Phospholipids. These are mixed glycerides of higher fatty acids and phosphoric acid in which two OH groups of glycerol are esterified by fatty acids and third by some derivative of phosphoric acid. Lecithin is an example of phospholipid. These are usually present in cell membrane.



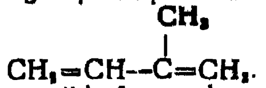
Phospholipid
(X=an aminoalcohol)



Lecithin

Waxes. Waxes are also included in the list of lipids. These are also esters of higher fatty acids. They, however, differ from oils and fats which are glycerides of higher fatty acids, in being esters of higher homologues of monohydric alcohols (See page 2·294).

Carotenoids. It is another group of lipids which are polymers



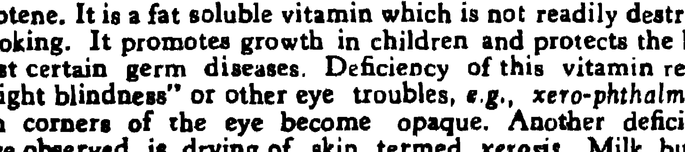
$CH_2=CH-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2$

of the hydrocarbon isoprene. $CH_2=CH-C(CH_3)=CH_2$. These are oil-soluble pigments which are responsible for producing red, yellow, orange and brown colours in various plant and animal materials, *e.g.*, tomatoes, carrots, pumpkins, egg-yolk, milk, butter, etc. β-Carotene ($C_{40}H_{56}$) is an important member of carotenoid family and occurs in carrots and green leaves. Another group of compounds called Xanthophylls is also included in carotenoids.

5. **Vitamins.**—In addition to the nutrients given above certain *organic substances required for regulating some of the body processes and preventing certain diseases are called* **vitamins.** Vitamins are organic compounds which cannot be synthesised by an organism. These are, therefore, an essential constituent of food for continued health and deficiency of any one of these in food causes one disease or the other. Several of these vitamins are known and are designated as vitamins A, B, C, D, E and so on. Many of these are now synthesised on a commercial scale and administered by doctors to their patients.

Different Vitamins and their Importance. Some important vitamins are :

(*i*) **Vitamin A, $C_{20}H_{29}OH$.** Chemically it is a derivative of



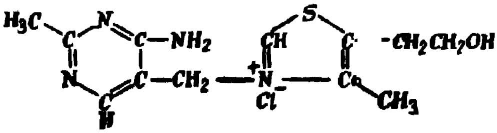
Vitamin-A ($C_{20}H_{29}OH$)

β-carotene. It is a fat soluble vitamin which is not readily destroyed by cooking. It promotes growth in children and protects the body against certain germ diseases. Deficiency of this vitamin results in "night blindness" or other eye troubles, *e.g.*, *xero-phthalmia* in which corners of the eye become opaque. Another deficiency disease observed is drying of skin termed *xerosis*. Milk, butter, cream, cheese, eggs, liver, vegetables and fruits constitute important sources of vitamin A.

(*ii*) **Vitamin B Complex.** It has now been found to be a mixture of a number of water soluble vitamins named as vitamins B_1, B_2, B_6 and B_{12}. These are not readily destroyed by cooking in the absence of baking soda. They help to regulate the nervous system.

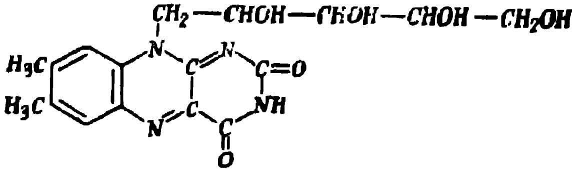
Lack of these vitamins causes beriberi, skin eruptions, loss of appetite, nervous disorders and pellagra. Milk, butter, whole grain, eggs, meat, green vegetables and brewer's yeast are good sources of vitamin B complex. Liver and kidneys also constitute a valuable source of these.

Vitamin B_1 is chemically thiamine. It is present in milk, green vegetables and rice polishings. Its deficiency causes beriberi and loss of appetite.



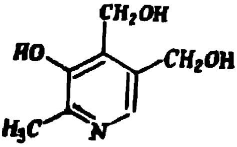
Vitamin B_1

Vitamin B_2 is chemically riboflavin present in milk, green vegetables and rice polishings. Its deficiency causes skin disorders and sore tongue.

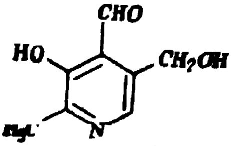


Vitamin B_2

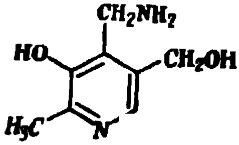
Vitamin B_6 is a mixture of three different compounds (closely similar ones)—pyridoxal (Y—CHO), pyridoxine (Y—CH_2OH) and pyridoxamine (Y—CH_2NH_2) where Y is the constituent C_7H_8N.



Pyridoxine



Pyridoxal

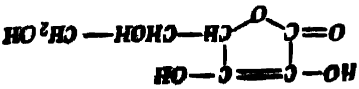


Pyridoxamine

These are present in cereal grains. Prolonged deficiency of vitamin B_6 causes convulsions and nervous disorders.

Vitamin B_{12} is a cyanocobalamin. Its molecule has a complex structure with a cobalt atom coordinated to four nitrogen atoms. It ocurs only in animals and micro-organisms. Its deficiency causes pernicious anaemia.

(iii) Vitamin C (*ascorbic acid*), C_6H_8O.



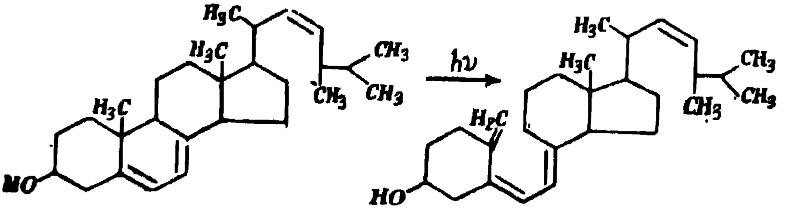
Vitamin C (Ascorbic acid)

It is a water soluble vitamin present in tomatoes, leafy vegetables, green peppers, citrus fruits (lemons, oranges, etc.), amla and papita. A deficiency of vitamin C causes structural defects of teeth and scurvy.

Vitamin C gets destroyed in contact with air and in alkaline media. Hence cooking of vegetables in open vessels or in presence of baking soda is not desirable.

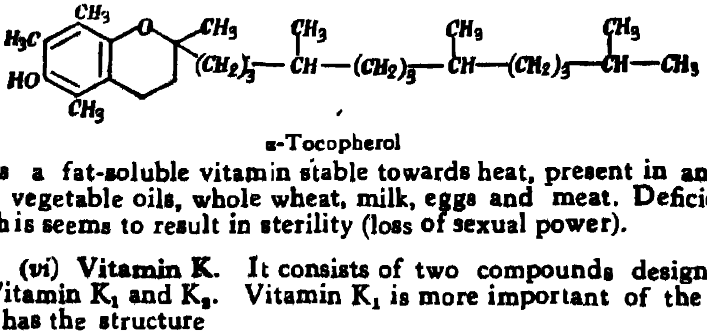
(*iv*) **Vitamin D** (*sunshine vitamin*). It is again a complex containing at least four different compounds designated as D_1, D_2, D_3, D_4, etc. Ultraviolet rays from the sun change ergosterol, present in human skin, into vitamin D_2 (hence the name *sunshine vitamin*)

Other known vitamins of this group are D_5, D_6 and D_7. A deficiency in this vitamin results in rickets, bending of legs like bows and poor formation of teeth. It is present in fish liver oil, milk and eggs.



Ergosterol Vitamin D_2, $C_{28}H_{44}O$ (Calciferol)

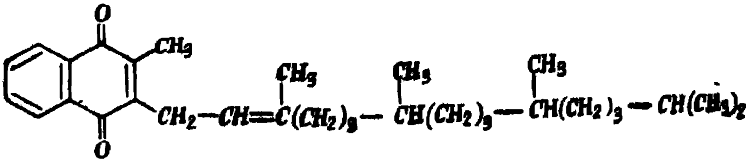
(*v*) **Vitamin E.** Vitamin E refers to a group of closely related compounds collectively called *tocopherols*. These are designated as α-, β-, γ-, δ-tocopherol, etc. α-Tocopherol is most active biologically (twice as active as β- or γ-tocopherol). α-Tocopherol, $C_{29}H_{50}O_2$ has the structure



α-Tocopherol

It is a fat-soluble vitamin stable towards heat, present in animal and vegetable oils, whole wheat, milk, eggs and meat. Deficiency in this seems to result in sterility (loss of sexual power).

(*vi*) **Vitamin K.** It consists of two compounds designated as Vitamin K_1 and K_2. Vitamin K_1 is more important of the two and has the structure



Vitamin K_1

It is present in leafy vegetables. Coagulating property of blood is due to the presence of vitamin K.

6. Enzymes.—Various reactions going on in biological systems are in many respects similar to ordinary reactions carried out by an organic chemist in a test tube. One significant difference between the two, however, is that the former takes place one hundred to one million times faster than the latter. Further these reactions occur at the body temperature (~310 K) and in the physiological pH range (~7). Catalysts employed by the cell to carry out these reactions are called enzymes.

Enzymes are complex organic catalysts produced by living cells. An enzyme is termed **intracellular** when it operates within the cell which produces it. It is designated **extracellular** when the site of its activity is outside the cell which produces it as in the case of gastric juices. *The substance on which an enzyme acts is termed its* **substrate.**

Enzymes are commonly named by adding the suffix *-ase* to the root of the name of the substrate or sometimes the products. For example, the enzyme acting on urea is termed *urease* and that acting on sucrose is named *sucrase.* Sucrase is also named *invertase* because the product in this case is invert sugar (a mixture of glucose and fructose). Some older names such as ptyalin, pepsin, trypsin and renin have been retained.

All enzymes are proteins. Some enzymes like pepsin and trypsin are simple proteins since their molecules are built entirely of amino acid units. Some protein molecules, however, contain a non-peptide part called a *prosthetic group.* Such proteins are known as *conjugated proteins.* For example, in haemoglobin the peptide part is globin and the non-peptide part (prosthetic group) is *hemin.* The two are held together by an amide linkage between COOH group of hemin and an NH_2 group of globin.

Many enzymes are conjugated proteins and thus contain prosthetic groups. The prosthetic group may be a metal or an organic group (a B-vitamin usually) or an organic group which includes a metal atom. For example, hemin in haemoglobin includes an iron atom.

The conjugated protein as a whole is termed *holoenzyme.* Its peptide part is known as *apoenzyme.* The non-peptide part is called *coenzyme* when it is a B-vitamin. It is termed *cofactor* when it is a metal. Thus we can express their mutual relation as follows :

$$\text{Holoenzyme} \rightleftharpoons \text{Apoenzyme} + \text{Coenzyme}$$

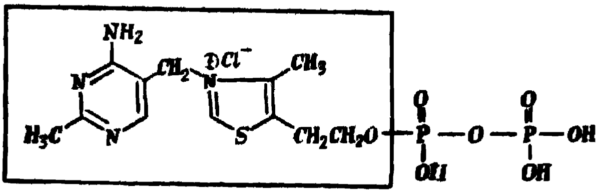
or $$\text{Conjugated protein enzyme} \rightleftharpoons \text{Peptide part} + \text{Prosthetic group}$$

Apoenzyme is sensitive towards heat in comparison to the coenzyme which is stable towards heat. Both these parts are, however, essential for the active functioning of the enzyme.

In most of the coenzymes the heterocyclic base of the nucleotide is substituted by another unit which is usually a derivative of some particular B-vitamin In some coenzymes there is no nucleotide attached.

All the water soluble B-vitamins are essential for the proper functioning of the body and must, therefore, be present in the diet we take. Undoubtedly the need for these substances is due to their function as prosthetic groups.

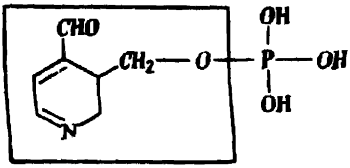
Two examples of coenzymes are :



Vitamin B_1 (Thiamine) Pyrophosphate part

Thiamine pyrophosphate (TPP)

(*a coenzyme*)



Pyridoxale (Vitamin B_6) Phosphate half

Pyridoxal phosphate (*a coenzyme*)

Mode of Enzyme Action. It is believed that a reaction catalysed by an enzyme occurs in two steps. In the first step a molecule of the enzyme (E) collides with a molecule of the substrate (S) to form an intermediate compound (E—S) which is termed **enzyme-substrate complex**. This step is a reversible one. In the second step the substrate in the complex changes into products (P) which then leave the surface of the enzyme.

(i) $S+E \rightleftharpoons E-S$

(ii) $E-S \rightarrow P+E$

The formation of enzyme-substrate complex occurs at a specific location on the surface of the enzyme. *The section of the enzyme surface which combines with the substrate to form E—S complex and at which the transformation of the substrate to products occurs is termed the* **active site** *of the enzyme.*

The conformations of the active site and the substrate are complementary due to which one fits into the other as a key fits into a lock. The lock and key theory explains the specificity of enzyme. Each enzyme catalyses only a particular reaction and not any and every reaction.

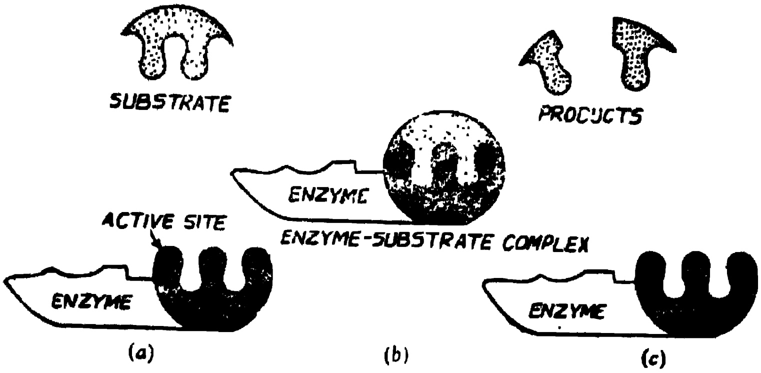


Fig. 54·1—A schematic representation of the *lock and key theory* of enzyme action. (*a*) The active site on the enzyme and the substrate have complementary structures, and, therefore, fit together like a key fitting in a lock forming an E—S complex. (*b*) Catalytic reaction occurs while the enzyme and substrate are bonded together in the E—S complex. (*c*) Products of the reaction leave the surface of enzyme which is now free to combine with another substrate molecule as in (*a*).

Factors influencing Enzyme Activity. Various factors which influence enzyme activity are :

(*a*) *Concentration of substrate.* The rate of enzymic reaction increases with increase in concentration of the substrate until a limiting rate is reached and further increase in concentration of substrate does not alter the rate of reaction.

At lower concentration formation of E—S complex is the rate determining step while at higher concentrations dissociation of E—S complex is the rate determining step.

(*b*) *Concentration of Enzyme.* Rate of reaction increases as the concentration of enzyme increases.

(*c*) *Temperature.* For every enzyme there is an optimum temperature at which its activity is maximum.

(*d*) *Hydrogen Ion Concentration.* Enzymes being proteins are sensitive to changes in *p*H of their environments. Very high or very low values of *p*H can cause denaturation of proteins. Narrow *p*H range over which an enzyme will exhibit maximum activity is termed **optimum pH**. In this range the E—S complex exists in its proper charged form. For most body fluids the optimum *p*H lies between 6 and 8. Gastric juice being acidic is a notable exception.

Enzyme Inhibition. Any physical change or a chemical reagent that denatures protein will inhibit (decrease) the rate of enzymic reaction. Temperature and changes in *p*H inhibit enzyme activity in general. This type of inhibition is referred to as **non-specific inhibition.**

Most poisons which inhibit the activity of only specific enzymes are termed **specific inhibitors.** These are of the following three types :

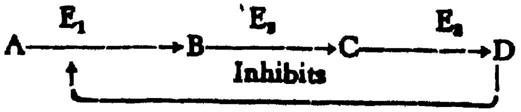
(*a*) **Competitive Inhibitor.** When there is a close structural resemblance between a certain substance (inhibitor) and a particular substrate, the two compete with each other for the active site on the substrate. The inhibitor, which does not undergo any transformation, remains bound to the enzyme and prevents the substrate molecules from approaching the active sites. This kind of inhibitor is called a **competitive inhibitor.**

Degree of competitive inhibition depends on the relative concentrations of substrate and inhibitor. At relatively higher concentration of inhibitor, it will block all active sites on the enzyme surface resulting in complete inhibition. The formation of inhibitor-enzyme complex being reversible, in presence of relatively higher substrate concentration, the inhibitor molecules are completely displaced from active sites and the inhibition is thus reversed.

The inhibition of the enzyme activity of *succinic acid dehydrogenase* by malonic acid (which resembles succinic acid in configuration) is a classical example of competitive inhibition.

(*b*) **Non-competitive Inhibitor.** *It is a substance which forms strong covalent bonds with an enzyme.* It cannot be displaced from the surface of the enzyme by adding excess of the substrate, *i.e.*, inhibition caused by this is irreversible. Some molecules of the inhibitor bind the enzyme at the active sites and thus prevent the substrate molecules from binding there. Some other molecules of the inhibitor bind the enzyme at points away from active sites and while doing so, they change the three-dimensional conformation of the active sites on the enzyme. As a result of this change substrate molecules can no more bind to these active sites.

(*c*) **End-product Inhibition.** In a biosynthetic pathway of the following type



E_1, E_2, E_3, are the enzymes catalysing various steps given above. The final product D is found to inhibit the enzyme E_1, *i.e.*, formation of B from A is inhibited. As a consequence the whole pathway is inhibited. This type of inhibition is termed end-product inhibition.

In all cases of such inhibition it has been shown that there are two distinct binding sites on the enzyme. One of these is for binding the substrate and the other for binding the inhibitory end product. The latter active site is known as *allosteric site.* When the inhibitory end-product binds to the allosteric site, there is a change in three-dimensional conformation of the enzyme. As a result the active site gets distorted and is rendered non-functional.

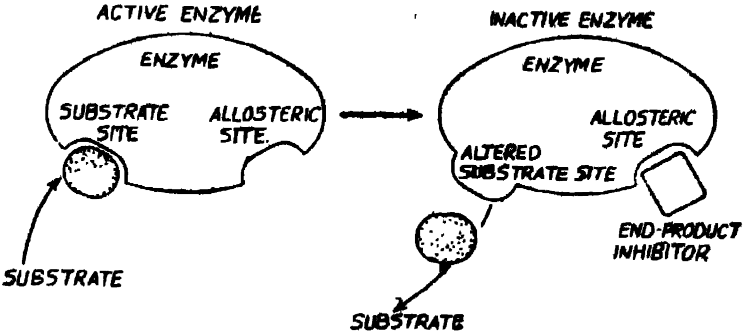
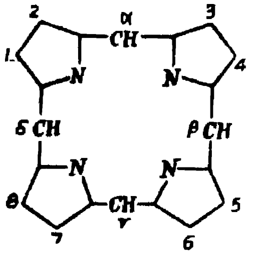
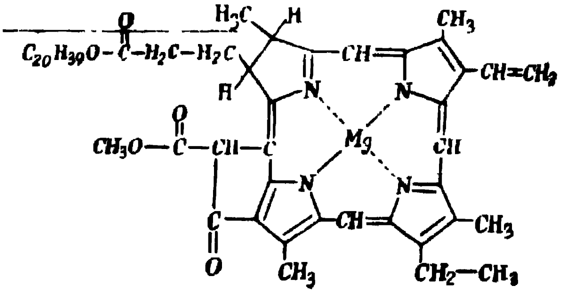


Fig. 54·2—Schematic representation of end-product inhibition caused by change in structural conformation preventing binding of substrate at the distorted substrate binding site.

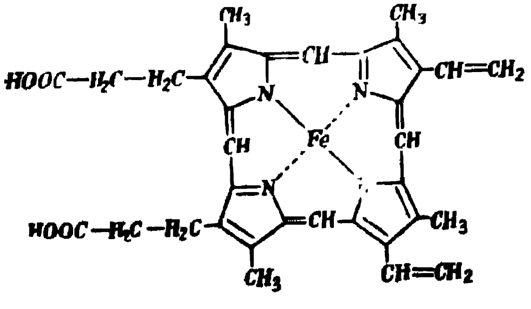
7. **Tetrapyrroles or Porphyrins.**—Green colouring matter of leaves is chlorophyll and red colouring matter of blood is termed heme which is part of haemoglobin responsible for carrying oxygen in blood. Cotchrome is an important compound present in the



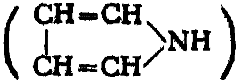
Porphyrin



Chlorophyll



Heme

respiratory system. Each one of these biochemically important compounds is made up of four pyrrole units  linked by four methine bridges (—CH=). These biomolecules are, therefore, collectively known as *tetrapyrroles* or *porphyrins.*

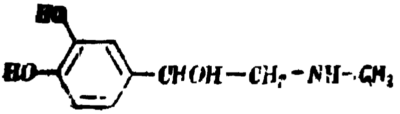
Basic porphyrin system and structures of chlorophyll and that of heme are given on page. 3.201

8. **Hormones.**—Hormones are secretions of endocrine (ductless) glands. These secretions are poured into blood as it passes through these glands. They have a regulatory influence on the chemical processes taking place in the body. Hormonal imbalance may result in metabolic disturbances like diabetes, goitre. It may result in growth alteration as in acromegaly (giantism). An imbalance in sexual hormones may result in malformation of sex organs. Pituitary is the master endocrine gland whose secretions (hormones) control the functioning of all other endocrine glands in the body. Adrenaline was the first hormone isolated and also the first hormone synthesised in the laboratory. Some important hormones present in the human body and their functions are summarized in the following Table :

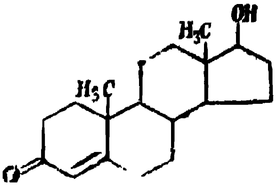
Table 54·1—Some Important Hormones

Hormone	Endocrine gland	Its functions
1. Adrenaline (Epinephrine)	Adrenal medulla	Maintenance of blood pressure; release of glucose from glycogen; release of fatty acids from fats.
2. Cartisone	Adrenal cortex	Regulation of metabolism of fats, proteins, carbohydrates, mineral salts and water.
3. Testosterone	Testis	Regulates normal functioning of sex organs in males.
4. Estrone and Estradiol	Ovary	Regulates normal functioning of sex organs in females.
5. Insulin	Pancreas	Regulates metabolism of glucose.
6. Pituitary hormones	Pituitary gland	Stimulation and control of functioning of all other endocrine glands in the body.
7. Thyroxine	Thyroid gland	Controls the various catabolic processes in the body involving burning of, fats, proteins and carbohydrates to liberate energy.
8. Parathyroxin	Para-thyroid gland	Controls the calcium and phosphorus metabolism in the body.

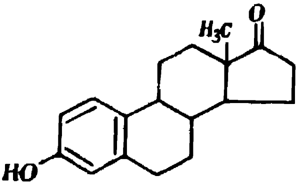
Structures of some hormones are given below :



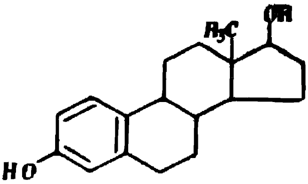
Epinephrine
(Adrenalin)



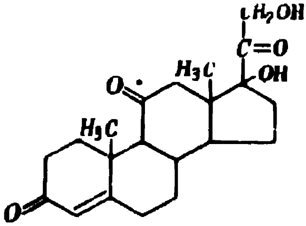
Testosterone



ESTRONE



ESTRADIOL



CORTISONE

9. **Proteins.** Among the most important and abundant substances which make up the living organisms are the compounds called proteins. These have a variety of functions in the body. Some of these are fibrous and are the main components of the hair, muscles and skin. A number of them are present in the body fluids and serve as carriers of inorganic and organic compounds. We are familiar with enzymes which act as catalysts and control many biochemical reactions which make it possible for us to live. These are protein catalysts. It is an essential constituent of our food. Animals can live without fats and carbohydrates for a long time but not without proteins. They require proteins for growth (*i.e.*, for building new cells) and maintenance (*i.e.*, for replacement of proteins lost by wear and tear of tissues). The name *protein* was derived from the Greek word *protios* (meaning to *take the first place*).

Plants build up their proteins from carbon dioxide, water, mineral salts in the soil (nitrates and ammonium salts) and solar energy. Animals derive their proteins ultimately from plants. Animals eat plants and during the process of digestion the plant proteins are hydrolysed by enzymes producing amino acids which are absorbed by blood and reach the various tissues. The animal proteins are synthesised from these amino acids. These have been discussed at length in Chapter 50.

10. Digestion of Food.—Living beings need energy for their maintenance and growth. It may be derived from environments as plants do from the sun or may be obtained by assimilation of food as in animals. Raw food may be taken as such or after cooking. It is chewed in the mouth and swallowed when it passes through a long passage in the body called alimentary canal. During this passage it gets mixed with various enzymes in different parts of the alimentary canal. This converts the various constituents of food (proteins, carbohydrates and fats) into their simpler forms which can be carried by blood to different parts of the body for utilisation.

The hydrolytic process in which various constituents of food are broken down into simpler chemical units which can be absorbed by the body is termed **digestion.** In human body digestion takes place in the alimentary canal and absorption occurs primarily in the small intestines.

Changes taking place in different parts of the body and the enzymes responsible at various steps are summarized in the following table :

Part of the alimentary canal	Name of secretion	Enzyme present	Action
1. Mouth	Saliva	Amylase (ptyalin)	Hydrolyses starch into maltose.
2. Stomach	Gastric juice	Pepsin, acts in the presence of HCl present ; ($pH=2$)	Hydrolyses proteins into proteoses and peptones.
3. Small intestines (*All juices being poured into these are alkaline* ($pH=7{\cdot}5$).	(*a*) Bile from liver	bile salts	Emulsifies the fats, *i.e.*, breaks bigger fat droplets into smaller ones and checks growth of bacteria.
	(*b*) Pancreatic juice	(*i*) lipase	Hydrolyses fats into fatty acids and glycerol.
		(*ii*) amylase	Hydrolyses starch into disaccharides (maltose).
		(*iii*) trypsin	Hydrolyses proteins, proteoses and peptones into simpler peptides.
	(*c*) Intestinal juice	(*i*) lipase	Same as before.
		(*ii*) maltase	Converts disaccharides (maltose etc.) into monosaccharides (glucose).
		(*iii*) trypsin and chymotrypsin	Hydrolyses partially digested proteins into small peptide fragments.
		(*iv*) peptidases	Convert peptides into amino acids.

Thus we find that in the small intestines the digestible portions of food get completely digested. After digestion these are present as glucose, amino acids, fatty acids, glycerol along with vitamins and minerals. These pass through the mucous membrane of the intestines and get absorbed by blood stream which carries these two different body cells where assimilation of food takes place.

A part of the food is converted into energy required for various body functions. Another part is used for the synthesis of proteins required for building tissues necessary for growth or for replacement of old worn out ones. The food taken in excess of these requirements is stored in the body as glycogen (animal starch) in the liver or as fat which gets deposited in different parts of the body.

Undigestible parts of the food along with undigested ones and various secretions find their way into the *intestines or rectum* from where these are excreted in the form of faeces.

Digestion of Food at a Glance

$$\textbf{Proteins} \xrightarrow[\textit{(gastric juice)}]{\text{pepsin}} \begin{matrix}\text{Proteoses}\\ \text{and}\\ \text{peptones}\end{matrix} \xrightarrow[\textit{(Pancreatic \& intestinal)}]{\text{trypsin \& chymotrypsin}} \text{Peptides} \xrightarrow[\text{intestinal}]{\text{peptidases}} \begin{matrix}\textbf{Amino}\\ \textbf{Acids}\end{matrix}$$

$$\begin{matrix}\textbf{Polysaccharide}\\ \text{(Starch)}\end{matrix} \xrightarrow[\text{pancreatic, intestinal)}]{\text{amylases (salivary,}} \begin{matrix}\text{Disaccharides}\\ \text{(maltose, etc.)}\end{matrix} \xrightarrow{\text{maltase}} \begin{matrix}\textbf{Monosaccharides}\\ \text{(Glucose, etc.)}\end{matrix}$$

$$\textbf{Fats} \xrightarrow[\text{salts}]{\text{bile}} \text{Emulsified fat} \xrightarrow[\text{pancreatic, intestinal)}]{\text{lipases (gastric,}} \begin{matrix}\textbf{Fatty Acids}\\ \textbf{+Glycerine}\end{matrix}$$

Metabolism. The term metabolism is used for various chemical processes involved in digestion of food in living organisms. It is termed **catabolism** when metabolic reactions involve degradation of absorbed food substances into smaller molecules. In the case of metabolic reactions involving biosynthesis of complex molecules from simpler ones it is termed **anabolism.** The term **metabolite** is used for any chemical compound that is involved in a metabolic reaction.

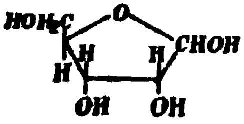
NUCLEIC ACIDS

11. **Chemical Genetics.**—Mendel is considered the founder of the science of genetics. As a result of his study of the inherited characteristics in pea plants he discovered in 1866 that mysterious "unit factor" called gene was responsible for the transference of characteristic from one generation to the other. Later on it was shown by T H. Morgan and others that genes are carried by physical structures called *chromosomes*. Genes are strung in a linear arrangement along chromosomes. In humans there are 46 chromosomes that carry the genes responsible for heredity. Nothing was known about the molecular structure of genes in 1950s. In the following decade, however, there was an explosion in

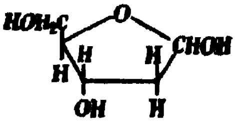
molecular biology and now we know a lot about the genes and their functions. Genes are made up of nucleic acids.

12. Nucleic Acids.—Nucleic acids are high molecular weight polymers. The monomer is termed a *nucleotide*. A nucleotide consists of three parts : (i) a phosphate group, (ii) a pentose sugar, and (iii) a heterocyclic base. These were first isolated from nuclei of pus cells in the nineteenth century and hence named nucleic acids. Now it is known that these are constituents of practically all cells.

Sugars in Nucleic acids. The pentose sugars present in nucleic acids are *ribose* and *deoxyribose*.

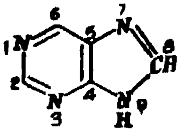


S-ribose

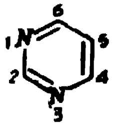


2-Deoxy-S-ribose

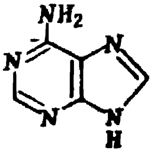
Heterocyclic bases in Nucleic acids. Some of the heterocyclic bases (derivatives of purine and pyrimidine) present in nucleic acids are cytosine, uracil, thymine (three derivatives of pyrimidine), adenine and guanine (two derivatives of purine).



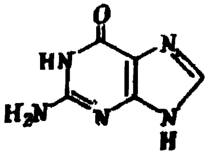
Purine



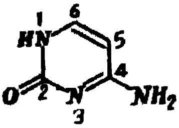
Pyrimidine



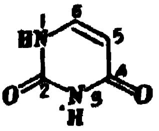
Adenine
(6-aminopurine)



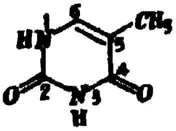
Guanine
(6-oxo-2-aminopurine)



Cytosine
(2-oxo-4-amino-pyrimidine)

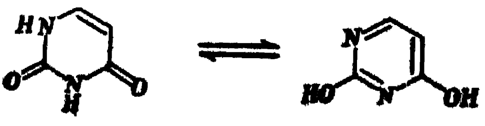


Uracil
(2, 4-dioxo-pyrimidine)



Thymine
(2, 4-dioxo-5-methyl-pyrimidine)

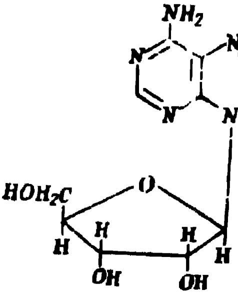
Oxygen-containing bases given above in the keto (lactam) form exist as the enol (lactim) form as well.



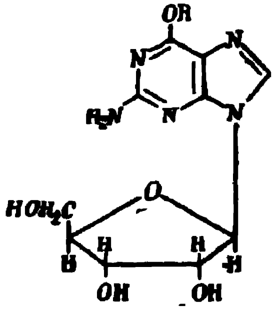
Lactam form Lactim form

However, the resonance energy of the amide groups present in the lactam form is generally greater than the resonance stabilisation of the aromatic ring in the lactim form. The base joined to sugar in a nucleoside is, therefore, present in the lactam form and also predominates at $pH \sim 7$.

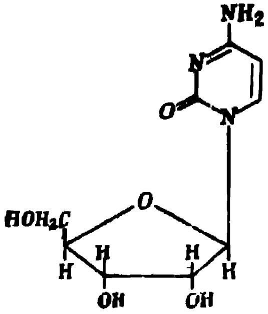
Nucleosides. A base joined to a sugar molecule is termed as *nucleoside*. These base-sugar molecules are so named as to reflect the names of the base and sugar present. For example, adenosine (ribose+adenine), guanosine (ribose+guanine), cytidine (ribose+cytosine) and uridine (ribose+uracil).



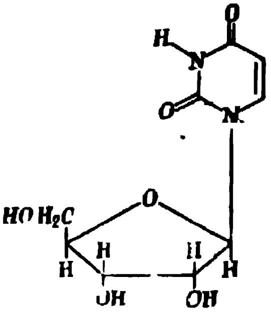
Adenosine
(ribose+adenine)



Guanosine
(ribose+guanine)



Cytidine
(ribose+cytosine)

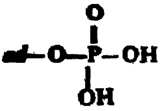


Uridine
(ribose+uracil)

Nucleosides obtained by substituting ribose by deoxyribose in three of the above are deoxyadenosine, deoxyguanosine and deoxycytidine.

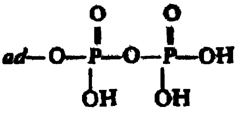
Problem —Draw the structural formulae of the three nucleosides containing deoxyribose.

Nucleotides *Nucleoside phosphates are called nucleotides.* These may be mono-, di- or tri-phosphate. For example, adenosine gives adenosine monophosphate (AMP), adenosine diphosphate (ADP) and adenosine triphosphate (ATP).



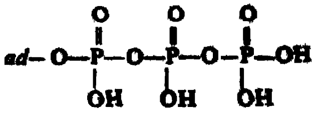
$$ad{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}{-}OH$$

AMP



$$ad{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}{-}OH$$

ADP



$$ad{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}{-}OH$$

ATP

(*ad* is an abbreviation for adenosine).

The —P—O—P— bonds are high-energy phosphate bonds and it is on account of these bonds that some nucleotides act as energy carriers.

Depending upon the type of pentose (ribose or deoxyribose) present, the nucleotides can be of two types : *ribonucleotides* and *deoxyribonucleotides*.

Nucleotides are the building blocks of the high molecular weight polymers, polynucleotides called nucleic acids. Thus nucleic acids can be diagrammatically represented as follows :

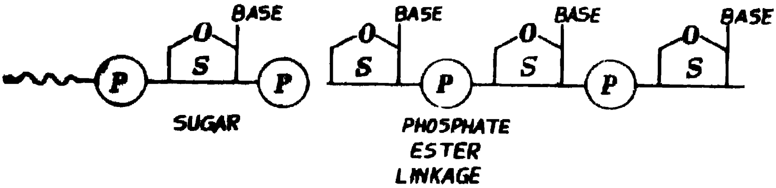


Fig. 54·3—Diagrammatic representation of nucleic acids—polymer of nucleoside phosphates.

Functions of Nucleotides. Three crucial functions of nucleotides present in the cells are :

(i) Some of these are energy carriers.

(ii) Some others are co-enzymes.

(iii) Some of them are carriers of hereditary information—the genetic code.

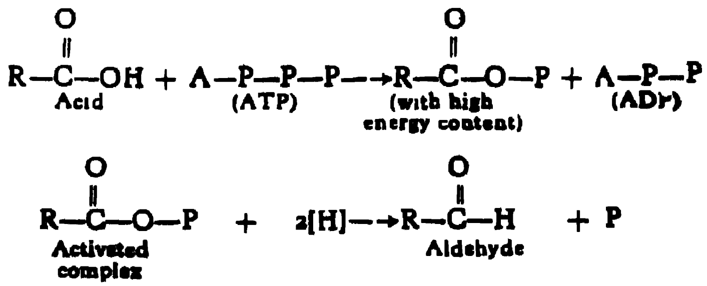
13. Nucleotide as Energy Carriers.—The —P—O—P— bonds in a nucleotide, *e.g.*, adenosine diphosphate (abbreviated as A—P—P) or adenosine triphosphate (abbreviated as A—P—P—P) are high energy phosphate bonds. When a new bond is formed energy is absorbed and when a bond is broken, energy is released.

$$\underset{\text{(ATP)}}{A{-}P{-}P{-}P}\xrightarrow{H_2O}\underset{\text{(ADP)}}{A{-}P{-}P}+P\ ;\ \Delta G_{298}\ (pH,\ 7{\cdot}0)=-31{\cdot}8\ \text{kJ}$$

$$\underset{\text{(ADP)}}{A{-}P{-}P}\xrightarrow{H_2O}\underset{\text{(AMP)}}{A{-}P}+P\ ;\ \Delta G_{298}\ (pH,\ 7{\cdot}0)=-31{\cdot}8\ \text{kJ}$$

During synthesis of ADP and ATP in the cell energy is absorbed. Required energy is derived from oxidation of carbohydrates and fats. Primary function of respiration is to produce ATP from ADP. ATP is the most important nucleotide functioning as energy carrier in living cells. Other nucleotides play only a limited role as energy carriers. When energy is required for any body function, ATP changes into ADP liberating the required energy.

Some reactions thermodynamically impossible in the laboratory are accomplished in the body with the help of ATP. For example, reduction of RCOOH to RCHO is a thermodynamically impossible reaction but accomplished in the living system at room temperature and at $pH\sim7$.



$$\underset{\text{Acid}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-OH} + \underset{\text{(ATP)}}{A-P-P-P} \longrightarrow \underset{\text{(with high energy content)}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-O-P} + \underset{\text{(ADP)}}{A-P-P}$$

$$\underset{\text{Activated complex}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-O-P} + 2[H] \longrightarrow \underset{\text{Aldehyde}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-H} + P$$

ATP increases energy content of R—COOH by transferring its one phosphate group to it and thus forming an activated complex which is next reduced to an aldehyde.

14. **Principal Types of Nucleic Acids.**—Polynucleotides composed of nucleotides joined by means of phosphate ester linkages are known as *nucleic acids*. Nucleotides are nucleoside phosphates. Sugar present in the nucleoside may be ribose or deoxyribose. Based on the nature of sugar molecule present, the nucleosides are of two types ; ribonucleosides and deoxyribonucleosides. Their phosphates (nucleotides) are called ribonucleotides and deoxyribonucleotides respectively. Corresponding to these two types of nucleotides, nucleic acids (polynucleotides) are of two types :

(i) Those consisting of ribonucleotides are called *Ribonucleic acids* (RNA).

(ii) Those consisting of deoxyribonucleotides are known as *Deoxyribonucleic acids* (DNA).

Both DNA and RNA contain two bases of the purine family, adenine and guanine, along with one pyrimidine, cytosine. However, they differ from each other in respect of the fourth base present in each. DNA contains thymine whereas uracil is present in RNA. The molecular mass of RNA (range 10^4—10^6) is less than of DNA (range 10^6—10^9).

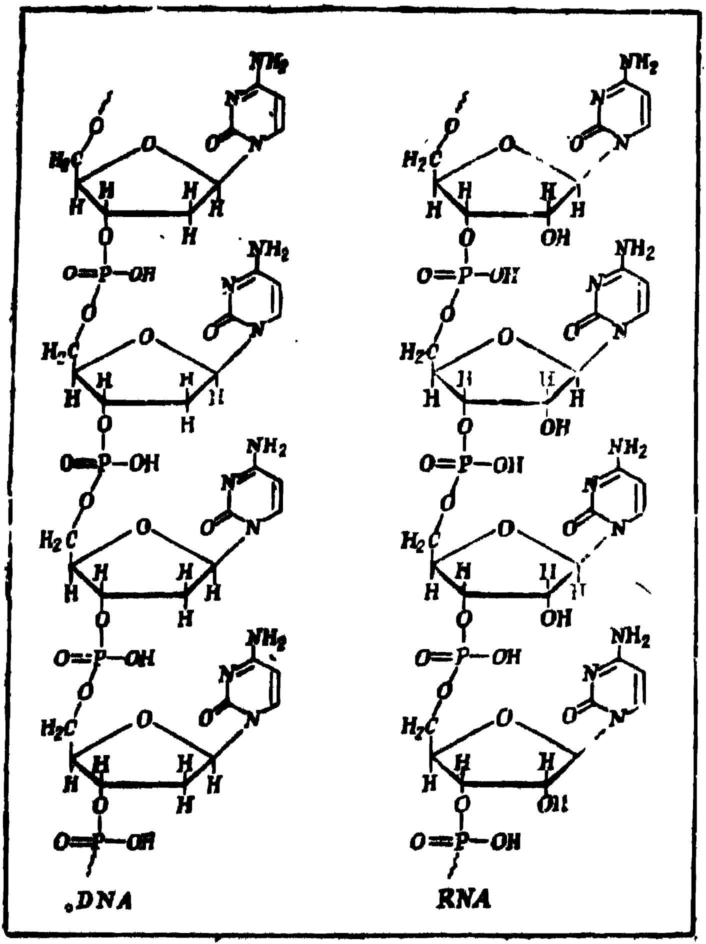
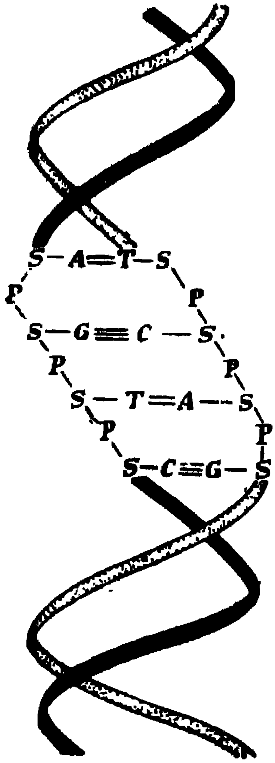


Fig. 54·4—Examples of DNA and RNA.

15. Structure of DNA.—Based on the chemical and physical evidence, DNA molecule is believed to be a double right-handed helix made up of two polynucleotide chains wound round the same axis like a spiral staircase. The two chains of the double helix are held in position by hydrogen bonds between base residue in one chain and appropriate base residues in the neighbouring chain. It has been suggested specifically that guanine (G) is linked to cytosine (C) by three hydrogen bonds and adenine (A) is linked to thymine (T) by two hydrogen bonds. We can abbreviate these base pairings as G≡C and A=T respectively.



Abbreviation used:

P=Phosphate diester

S=Sugar (deoxyribose)

(G≡C)=guanine-cytosine pairing

(A=T)=adenine-thymine pairing.

Fig. 54·5—Double-helix structure of DNA with abbreviated representation of hydrogen bonding between bases.

16. **Replication of DNA.**—DNA molecule has the unique property of replication—building up another identical molecule. During replication the double-stranded helix of DNA separates into two single strands. Each single strand then synthesises its appropriate complementary strand resulting in the formation of two double-stranded DNA molecules. Due to the unique specificity of the G≡C and A=T base pairings, the newly synthesized complementary strand in each case is a carbon copy of the strand originally separated from it. Thus in each resulting double-stranded DNA molecule, one of the strands comes from the parent DNA molecule, and the other is newly synthesized. Further each resulting molecule is an exact replica of the parent DNA.

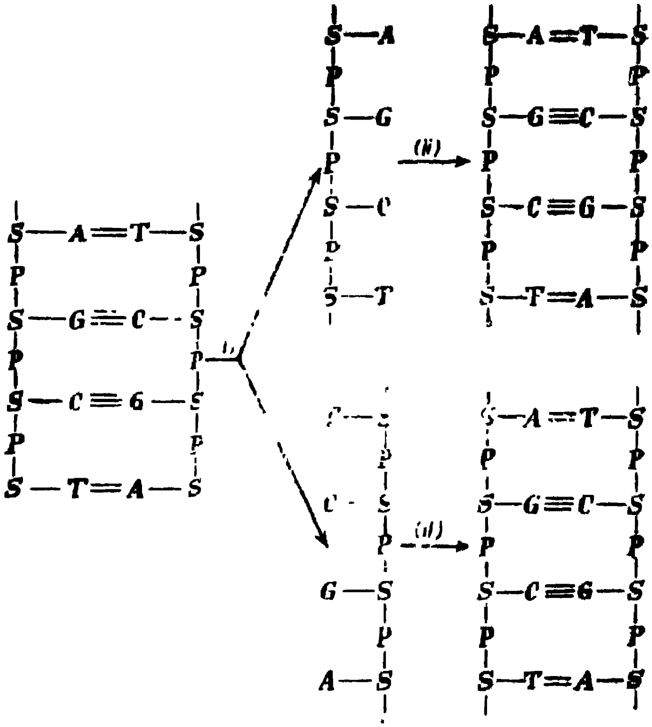


Fig. 54·6—Schematic representation of DNA replication. Step (i) involves separation of double-stranded helix of parent DNA into two single strands. Step (ii) involves synthesizing of complementary strand for each to form complete DNA molecule exact replica of the parent DNA.

17. Functions of DNA.—DNA is often referred to as the 'master molecule' because of the key role it plays in the living cell. Three important functions performed by DNA are :

(i) It sends information and instructions to the cell for the manufacture of specific proteins.

(ii) Due to its unique property of self-replication it is responsible for maintaining heredity traits from generation to generation.

(iii) Under certain conditions, *e.g.*, when exposed to X-rays, γ-rays or ultraviolet light or under the action of certain chemicals, DNA may undergo mutations, *i.e.*, its base sequence may undergo slight alteration. These changes are passed on to the near replicated molecules which bring about changes in the structure and functioning of the cell. This brings about certain changes in the animal and its progeny.

18. Structure and Functions of RNA.—Similarities and differences between DNA and RNA were given on page 3·209.

Another difference between the two is that RNA is a single-stranded molecule. Three principal kinds of RNA are found in living cells :

(i) *Ribosomal* RNA (rRNA) is present in ribosomes and constitutes about 80% of the total RNA. Its molecular mass is $\sim 100 \times 10^4$ and it is metabolically stable

(ii) *Transfer* RNA (tRNA) *or soluble* RNA (sRNA) occurs in soluble cytoplasm and constitutes about 15% of total RNA. Its molecular mass is $\sim 2{\cdot}5 \times 10^4$ and it is important in amino acid transport.

(iii) *Messenger* RNA (mRNA) occurs in ribosomes, cytoplasm and constitutes about 5% of total RNA. Its molecular mass is 50×10^4 and has a very short life. It is a complementary copy of a segment of one strand of DNA For example, if the base sequence in the RNA strand is

—A—T—C—G—A—A—T—

the base sequence in the mRNA would be

—U—A—G—C—U—U—A—

In RNA, uracil (U) is used in place of thymine (T) present in DNA.

RNA is believed to be a single-stranded molecule looped back on itself to form a helical structure. In the helical portion, the base pairing is possible but the bases present along the loop cannot be paired. RNA molecules vary in size and in number of loop-and-helix units.

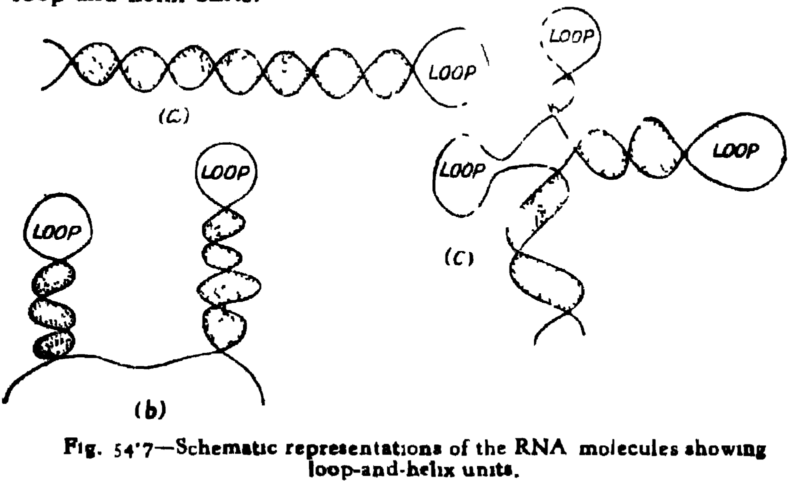


Fig. 54·7—Schematic representations of the RNA molecules showing loop-and-helix units.

Biological Function of RNA. RNA helps in the biosynthesis of proteins (see next section). There are indications that RNA may in some way be associated with the process of learning and memory storage.

19. **Biosynthesis of Proteins.**—Biosynthesis of proteins in the cell is taking place in the following steps :

(i) A chain of DNA, called gene, transmits messages to protein factories (ribosomes) in the cytoplasm. DNA in the nucleus serves as a template for the synthesis of an mRNA molecule (a complementary copy of DNA segment, as discussed earlier).

(ii) The mRNA so synthesised diffuses out of the nucleus to the cytoplasm and gets attached to a ribosome (a sub-cellular structure). There it itself serves as a template for protein synthesis.

The function of mRNA is to direct the synthesis of a specific protein chain. This is possible because *each group of three base along the mRNA strand now specifies a particular amino acid and the sequence of these triplet groups determines the sequence of the amino acids in the protein.* Since the code involves three bases for coding unit, it is termed a triplet code whereas the coding unit is referred to as a codon. The codon controls the incorporation of one specific amino acid at a particular position in the protein chain.

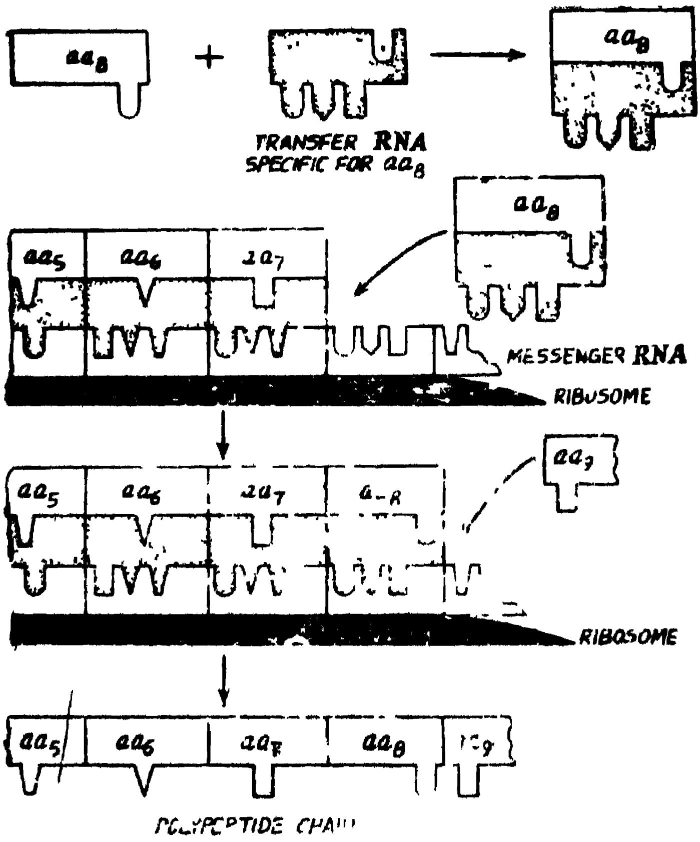


Fig. 54·8—Schematic representation of biosynthesis of protein involving tRNA and mRNA on the surface of the ribosomes. The chain may stay on the surface of ribosome till completion of the polypeptide chain

(iii) The amino acid is first attached to a *t*RNA which carries it to the correct site on the *m*RNA template. This *t*RNA has a base sequence complementary to the three-base sequence on the *m*RNA. One amino acid after the other is thus transported to the site. This is followed by formation of amide bonds under the influence of appropriate enzyme and thus the synthesis of a polypeptide chain is completed.

Thus we find that genetic information passes within the same cell from DNA to RNA and then on to protein. Similar genetic information passes from the parent DNA to a daughter DNA.

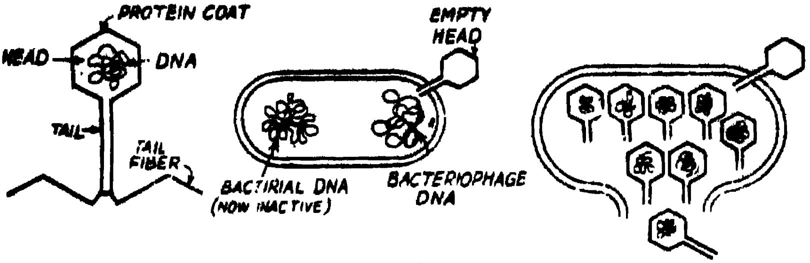
$$\begin{tikzcd}
\text{(Parent cell)} & \text{DNA} \arrow[r, "\text{Step A}"] \arrow[d, "\text{Step R}"'] & \text{RNA} \arrow[r, "\text{Step B}"] & \text{Protein} \\
\text{(Daughter cell)}\ \textit{First generation} & \text{DNA} \arrow[r, "\text{A}"] \arrow[d, "\text{R}"'] & \text{RNA} \arrow[r, "\text{B}"] & \text{Protein} \\
\textit{Second generation} & \text{DNA} \arrow[r, "\text{A}"] & \text{RNA} \arrow[r, "\text{B}"] & \text{Protein}
\end{tikzcd}$$

Step A shown in the above diagram (DNA → RNA) is termed *transcription step* whereas step B (RNA → Protein) is called *translation step*. Step R in which genetic information passes from the parent DNA to daughter DNA is known as the *replication step*

20. **Viruses.**—Diseases like common cold, influenza, encephalitis, rabies, cowpox, smallpox and measles are caused by viruses. A virus is essentially DNA or RNA (never both) protected by a coat of protein. Recall that the cells of higher organisms, from bacteria to man, contain both DNA and RNA. Viruses differ from one another in shape and size. For example, these may be spherical, rod-shaped and shaped like threads Influenza virus is about ten times as big as polio virus.

Important characteristic of viruses is their infectivity. The protein coating helps the virus to penetrate the cell wall of specific hosts. Viruses do not have the necessary biological machinery to replicate on their own. Thus outside the host cell a virus is simply an inert chemical complex. However, after entering the host cell it can use the cell's mechanisms for nucleic acid replication as well as protein synthesis to produce more virus particles. As their number increases the cell bursts and gets destroyed. The virus particles then enter other cells and cause their destruction.

Viruses have only a limited host range and cannot infect all types of host cells. For example, a virus which can infect a certain species of rodent may be harmless to another related species of the same.



(a) (b) (c)

Fig. 54·9—Life cycle of a typical virus. (a) Drawing of a virus, DNA located in the head of the particle, is surrounded and protected by protein coat. (b) During infection DNA is injected into a bacterial cell and uses the machinery of the cell to synthesise more virus particles. (c) When sufficient number of virus particles have been manufactured, the cell bursts.

21. **Biological Aspects of Ageing.**—All living organisms grow old with passage of time. Old age is accompanied by weakening of the functioning of various organs of the body in addition to the skin getting wrinkled. The process of growing old is called *ageing*.

A lot of research is being carried out to find out causes of ageing so that if somehow the process could be retarded. Various plausible causes responsible for the ageing process are :

(*i*) According to one view DNA of each cell undergoes self-destruction after a fixed interval leading to ageing.

(*ii*) According to another theory the cells age and ultimately die on account of certain environmental causes like damage of DNA by various radiations. This leads ultimately to the destruction of cells.

(*iii*) Still another view put forward is that with passage of time waste materials accumulate inside or around the living cells. This hinders the proper functioning of these cells and sets in the ageing process.

It is quite likely that the process of ageing may be the result of combination of a number of factors. However, in the absence of any conclusive evidence, ageing process is still a matter of speculation.

QUESTIONS

Essay Type :

1. What do you understand by a living system ? Why do living organisms need energy ? How do they get this energy ?

2. What are carbohydrates ? How are they classified ? What is their importance in living systems ?

3. Write a short essay on vitamins and their importance.

4. Define, explain or give an example of the following :

(*i*) enzyme, (*ii*) apoenzyme, (*iii*) coenzyme,
(*iv*) holoenzyme, (*v*) substrate, (*vi*) active site,
(*vii*) allosteric site, (*viii*) optimum pH, (*ix*) inhibitor,
(*x*) enzyme specificity, (*xi*) optimum temperature.

5. What are fats and oils ? What is their importance to the living systems ?

6. What do you know about the mode of enzyme action ?

7. Discuss the various factors influencing enzyme activity.

8. Write a short essay on 'enzyme inhibition'.

9. In what ways are enzymes similar to ordinary chemical catalysts ? How do they differ ?

10. What are hormones ? What is their importance in the human system ? Name any four hormones and give their functions.

11. What are proteins ? Discuss their role in living systems.

12. Write a paragraph on digestion of food.

13. How may different polypeptides differ from one another ? What do you know about the spiral structure of proteins ?

14. Write a note on uses of proteins.

15. How do you say that nucleotides are energy carriers ?

16. What are nucleic acids ? What do DNA and RNA stand for ? What are points of difference between the two ?

17 What do you know about the structure of DNA ? What is meant by replication of DNA ?

18. What are various functions of DNA ?

19. What do you know about structure of RNA ? Name its various functions.

20 Write a note on Biosynthesis of proteins.

21. Write a note on viruses.

22 Heredity characteristics are encoded in the base sequence of DNA. Explain.

23. How do DNA and RNA differ (a) structurally, (b) in base composition, and (c) in function ?

24 Briefly outline the functional role of (a) DNA, (b) messenger RNA, (c) transfer RNA, and (d) ribosomal RNA in protein synthesis.

25. Write a short note on specificity and sensitivity of Enzymes.
(*Delhi B.Sc. Hons. 1979*)

26. Write short notes on : nucleoprotein and nucleic acid.
(*Delhi B.Sc. Hons. 1979*)

Short Answer Type :

1. What are biomolecules ? Name five classes of biomolecules.

2. What are lipids ?

3. What are phospholipids ?

4. What are waxes ?

5. What are carotenoids ?

6. What are vitamins ?

7. Write structural formula of vitamin A. Write three different sources of this and mention the diseases caused by its deficiency.

8. Write structures of vitamins B_1, B_2 and B_6.

9. Write six different sources of vitamin B-complex and mention various diseases caused by lack of vitamin B-complex.

10. Write chemical name and structural formula of vitamin C. Mention its sources and the diseases caused by its deficiency.

11. Write structural formula of vitamin D. Name various diseases caused by its deficiency.

12. Write structural formula of α-Tocopherol. It is a constituent of which vitamin ? Name one disease caused by its deficiency.

13. Write structural formula of vitamin K_1. Where does it occur ? Name one important function of this vitamin.

14. Define enzymes.

15. What is lock and key theory of enzyme action ?

16. Animals can digest starch but not cellulose. Explain.

17. Only a small fraction of the enzyme molecule binds to the substrate. What function is served by the remainder of the enzyme molecule ?

18. Explain why enzymes become inactive above and below the (*a*) optimum temperature and (*b*) the optimum pH.

19. What is the difference between a competitive inhibitor and non-competitive inhibitor ?

20. What are tetrapyrroles or porphyrins ?

21. Which was the first hormone isolated ?

22. Name the master endocrine gland. Why is it so called ?

23. Name any two hormones and give their functions.

24. What is a peptide linkage ?

25. What are the building blocks of proteins ? What are fibrous proteins ? Give two characteristics of these.

26. What are globular proteins ? Give two characteristics of these.

27. What is denaturation of proteins ?

28. Name two enzymes and write the reaction brought about by them

29. Name the various enzymes responsible for the digestion of proteins. What is the ultimate product ?

30. Name the various enzymes which help digestion of carbohydrates.

31. What is bile ? How does it help in digestion ?

32. Name the sugars present in nucleic acids.

33. Name the various bases present in DNA and RNA.

34. Define the terms nucleosides and nucleotides.

35. Name the sugar present in (i) DNA, and (ii) RNA.

36. What are various functions of nucleotide ?

37. Fill in the blanks :

The conjugated protein as a whole is termed...Its peptide part is known as......and non-peptide part is called......when it is a B-vitamin. It is termed.........when it is a metal.

[Hint. Select words from the list : Coenzyme, apoenzyme, cofacter and holoenzyme.]

38. Name various types of RNA.

39. What are viruses ? How do these cause disease ?

40. What is biological aspect of ageing ?

41. Give the names and formulae for all the compounds that can be obtained from the complete hydrolysis of DNA.

42. Name and draw the structural formulae of the pyrimidine and purine bases commonly found in nucleic acids.

43. Give structural formula for
(*a*) deoxyuridine, and (*b*) deoxyadenosine.

44. Give the structural formulae for dinucleotides composed of :
(*a*) cytosine and adenine
(*b*) thymine and guanine.

Show how these dinucleotides might link together through hydrogen bonds.

45. What is the relationship between each of the following ?
(*a*) ribose and deoxyribose,
(*b*) a nucleoside and a nucleotide,
(*c*) a nucleotide and nucleic acid,
(*d*) chromosomes, genes and DNA.

46. How many nucleotide units are present in a codon ?

47. Differentiate the viral processes of productive infection and cell transformation.

11

Chemistry in the Service of Man

CHEMOTHERAPY

1. Introduction.—Most of the diseases in man are caused by micro-organisms. Diseases may be avoided by preventing the entry of micro-organisms into the body. For this purpose we must kill and remove micro-organisms from articles of daily use and food. The process of making various articles free from these micro-organisms is termed sterilization.

If case the micro-organisms gain entry into the body, they multiply. If they overcome the body defences, they cause disease. Substance used for cure of an ailment or alleviation of symptoms is called a drug or medicine. Drugs may be a single chemical substance or a combination of two or more different substances. Each drug has an optimum dosage, below which it has no action and above this level it becomes a poison.

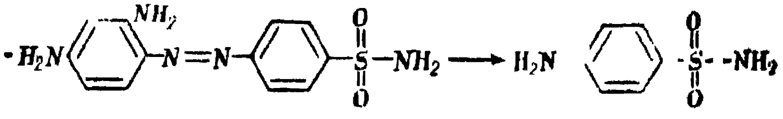
2. Chemotherapy.—*Chemotherapy is the use of chemicals (drugs) to selectively destroy infectious micro-organisms without simultaneously destroying the host.* It is a relatively modern phenomenon. Up to 1900 only three specific remedies were known. Mercury was used for curing syphilis but the results were often disastrous. Cinchona bark was an effective remedy for malaria and ipecacaunha was a specific cure for dysentery.

Modern chemotherapy began early in this century with the work of Paul Ehrlich who in his research sought to discover what he called *magic bullets*—drugs that would be toxic to infectious micro-organisms but harmless to humans. First milestone covered by him was his discovery in 1909 of salvarsan as a remedy for syphilis.

Ehrlich had observed with interest the ability of certain dyes to stain tissues selectively while he was a student of medicine. He thought some chemical reaction was involved between the tissue and the dye during staining. He pursued this idea in his research to discover certain dyes with selective affinities for micro-organisms. He hoped that some dye could be found which after modifications could be rendered specifically lethal to micro-organisms. Tens of thousands of chemicals including dyes were tested for their chemotherapeutic utility by Ehrlich and others between 1909 and 1935.

In 1935, the daughter of Gerhard Domagk, a doctor working in a German dye factory, suffered from a severe streptococcal infection contracted from a pin prick. As she was on death bed, Domagk gave her an oral dose of a dye called *prontosil* which had by that time been shown to inhibit the growth of streptococci in mice. The fever dropped quickly and the girl recovered within a short time. This amazing event not only saved the life of the girl, but also laid the foundation of modern chemotherapy. Domagk was awarded the Nobel Prize for medicine in 1939.

It was demostrated by the French scientist, Ernest Fourneau in 1936 that in the human body prontosil breaks down to produce sulphanilamide which is the actual active agent specifically lethal to streptococci.



Prontosil Sulphanilamide

Problem of finding a suitable drug for a particular disease has been tackled in the following three ways :

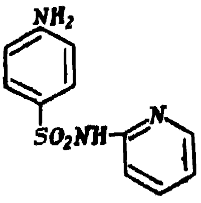
(*i*) By a method of trial and error. In this all kinds of compounds are tried for a particular disease and the one most effective is selected.

(*ii*) By studying the micro-organism responsible for the disease and finding the drug which inhibits its growth.

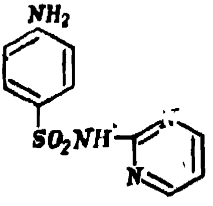
(*iii*) Improving the known drug found effective for various diseases. This is done by varying its structure till it becomes more effective. This method has been found to be most fruitful.

3. **The Sulpha Drugs (Sulphonamides).**—The sulpha drugs are derivatives of sulphanilamide and these were the first compounds found to be effective against pathogenic organisms or bacteria that cause pneumonia, tuberculosis, diphtheria, scarlet fever, gonorrhea, etc.

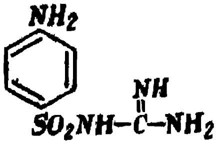
Fourneau's announcement about sulphanilamide being the actual active agent against streptococci, led to a search for other derivatives of sulphanilamide with better chemotherapeutic effects. Literally, thousands of chemical variations were obtained by varying the structure of sulphanilamide in almost every imaginable way. On testing all of these it was discovered that the best therapeutic results were obtained with those derivatives in which one hydrogen of the—SO_2NH_2 group was replaced by a heterocyclic amine or some other group. Some successful variations with best therapeutic results are given below :



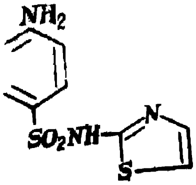
Sulphapyridine
(M and B 693)



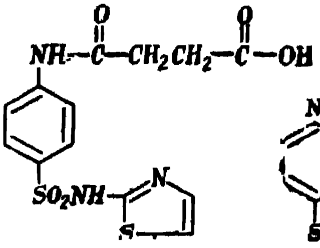
Sulphadiazine



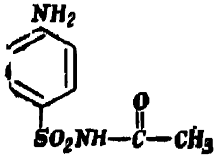
Sulphaguanidine



Sulphathiazole



Succinylsulphathiazole

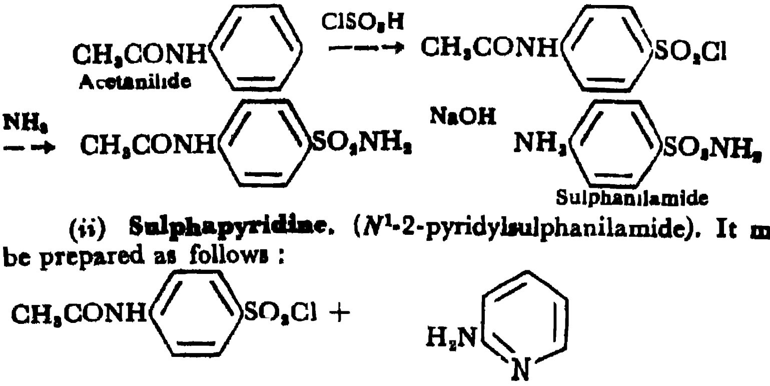


Sulphacetamide

Prior to 1938 thousands of people died of pneumonia every year. In 1938 sulphapyridine was found to be effective cure of the dreadful disease. In 1941, sulphacetamide was used successfully for curing urinary tract infections. In 1942, succinylsulphathiazole and phthalylsulphathiazole were found to be specific cure for gastrointestinal tract infections. Inside the body both of these are slowly hydrolysed to give sulphathiazole. Sulphathiazole saved the lives of thousands of wounded soldiers during the Second World War. Soldiers carried packages of sulpha drugs to sprinkle on the open wounds to prevent infection.

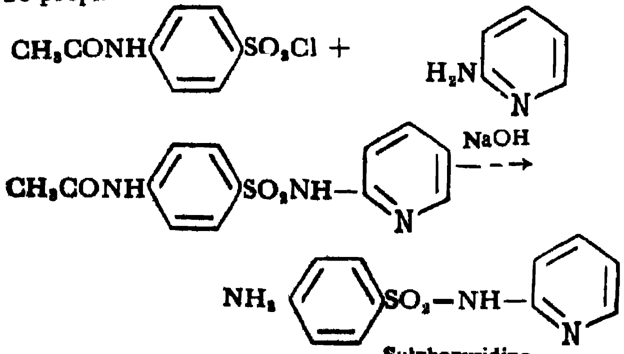
Synthesis of Various Sulpha dru.

(*i*) **Sulphanilamide.** It may be prepared from acetanilide.



Sulphanilamide

(*ii*) **Sulphapyridine.** (N^1-2-pyridylsulphanilamide). It may be prepared as follows :

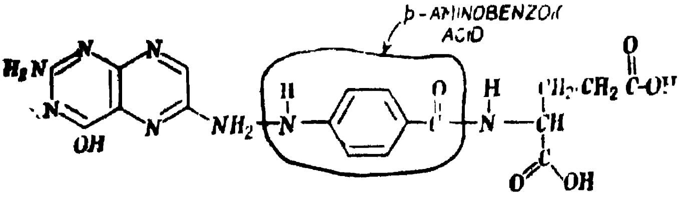


Sulphapyridine

(*iii*) **Sulphathiazole** (N^1-2-thiazolyl-sulphanide). In the above method used for sulphapyridine 2-aminopyridine is substituted by 2-aminothiazole to get sulphathiazole. It is more potent and less toxic than sulphapyridine. It is used mainly in severe infections.

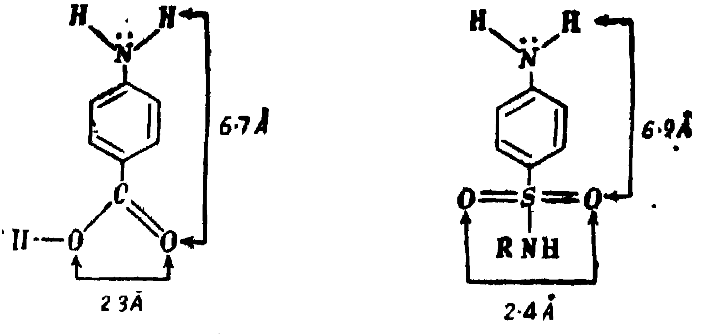
(*iv*) **Sulphadiazine** (*Sulphapyrimidine*). It is prepared by using 2-aminopyrimidine in place of 2-aminopyridine. It is widely used as a cure for mild infections.

Mode of Action of Sulpha drugs. All higher animals and a number of micro-organisms are unable to synthesize certain essential nutrients like vitamins, unsaturated carboxylic acids, certain amino acids, etc. *p*-Aminobenzoic acid is an essential nutrient for these bacteria which are sensitive to sulpha drugs. *p*-Aminobenzoic acid is needed by the enzyme within these bacteria for the synthesis of folic acid (another essential compound).



Folic acid

Drugs which inhibit the growth of any micro-organism, are termed *antimetabolites*. Sulpha drugs are antimetabolites for the bacteria, which need *p*-aminobenzoic acid for the synthesis of folic acid. Sulphanilamide acts as an inhibitor* for those enzymatic steps which are involved in the synthesis of folic acid by the bacteria. This is because the bacterial enzymes are unable to distinguish between the molecule of *p*-aminobenzoic acid and



p-Aminobenzoic acid A sulphanilamide

Fig. 55·1— Structural similarity of *p*-aminobenzoic acid and a sulphanilamide.

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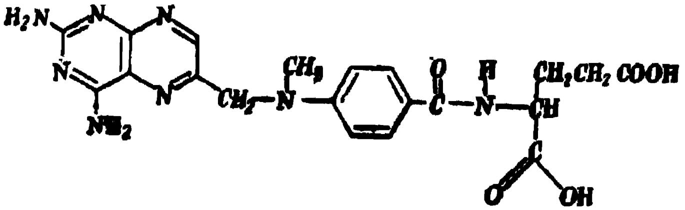
*In chapter 54 we have discussed the *active-site* concept of enzymatic catalysis. The active-site on the enzyme surface is a region which binds the substrate forming enzyme substrate complex which finally breaks to give the products. An inhibitor is a substance which competes with the normal substrate for the active site on the enzyme without themselves undergoing any chemical reaction. So long these inhibitor molecules are bound to the active sites, the enzyme cannot interact with the normal substrate. Thus the catalytic activity of the enzyme is blocked. Such inhibitors are termed *competitive inhibitors*. Sulpha drugs act as competitive inhibitors for the interaction of that of sulphanilamide, there being a close structural similarity between the two.

Sulphanilamide thus inhibits the activity of the bacterial enzyme which is, therefore, unable to synthesize requisite folic acid essential for living organisms resulting in the death of bacteria. Humans do not synthesize their own folic acid and get it from dietary sources. They are unaffected, therefore, by sulpha drugs.

Knowledge of this mode of action of sulpha drugs has led to the discovery of a large number of more effective antimetabolites. For example, *Methotrexate* has proved effective in the treatment of cancer. Methotrexate is a derivative of folic acid. By virtue of its resemblance to folic acid, it can enter certain reactions in place of folic acid but cannot serve the function of folic acid, *e.g.*, in the reactions involved in cell division. Thus methotrexate is toxic to all types of dividing cells but it is extremely toxic to cancer cells which divide most rapidly.



Methotrexate

4. **Antibiotics.**—*An antibiotic is a compound produced by one micro-organism that is toxic to another micro-organism.* The accidental discovery of penicillin, one of the most widely used antibiotics in the world, is one of the romantic stories of science. It is known that bacteria grows on nutrient agar surface. Agar is a gelatinous suspension prepared from seaweed. However, it was observed by Alexander Fleming in 1920s that bacteria does not flourish on nutrient agar in the region surrounding particular fungus, Penicillium notatum Westling. He suggested that this fungus produces an antibiotic named penicillin. In 1938, Ernst Chain and Howard Florey* isolated penicillin in pure form and proved its effectiveness as an antibiotic. It was introduced into medical practice only in 1941. Several naturally occurring penicillins have been isolated. All of these have the empirical formula

$$C_9H_{11}O_4SN_2R$$

In penicillin a four-membered ring is fused to another five-membered ring. Structures of individual penicillins are shown in Fig. 55·2. Penicillin G is the most commonly used one of these.

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*The three scientists received the Nobel Prize for Physiology and Medicine in 1945.

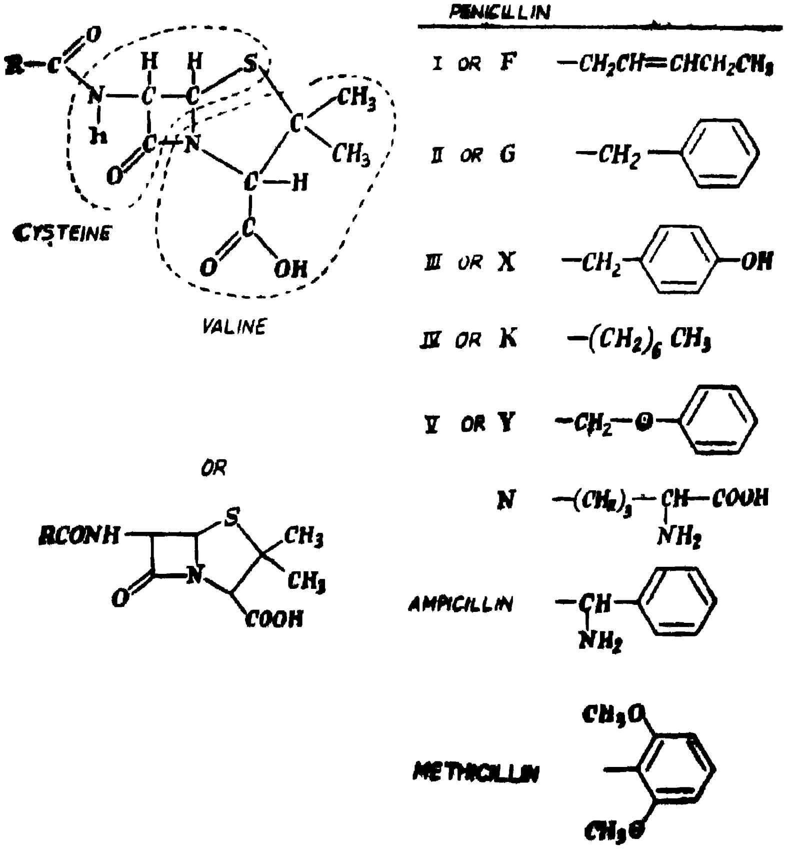


Fig. 55·2—In the molecule of penicillin two amino acids valine and cysteine are incorporated. Different penicillins differ from one another only in the nature of R.

Other Antibiotics. Penicillin cannot be administered orally since it is quite unstable and undergoes rearrangement to an inactive derivative in the acid pH of the stomach. Further, some kinds of bacteria develop resistance to penicillin by developing the enzyme penicillinase which breaks down the antibiotic. Some people are allergic to penicillin and the allergic reaction is sometimes very severe resulting in fatal coma.

To overcome these difficulties, scientists have discovered a number of other antibiotics. These have proved to be as effective as penicillin in destroying infectious micro-organisms. The commonly used ones of these are given below :

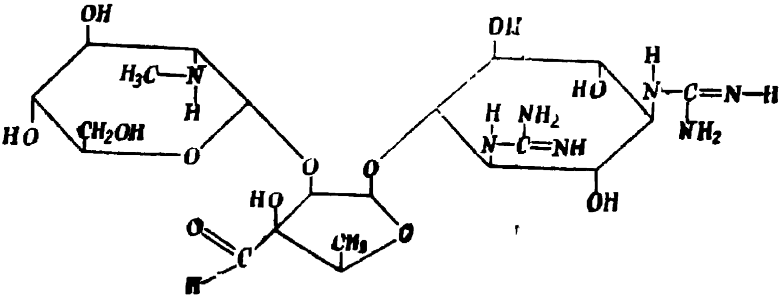
(*a*) **Streptomycin.** It was discovered by S.A. Waksman, Russian-born-American microbiologist, in 1944 as first antibiotic effective against tuberculosis. He was awarded the 1952 Nobel

Prize in Physiology and Medicine for this discovery. It is also used for other common infections like throat and lungs, ears and kidney.

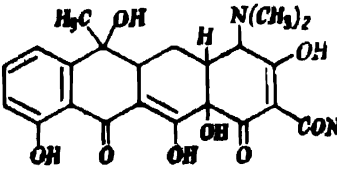
(*b*) **Tetracyclines.** Some other members of this group of antibiotics in addition to tetracycline are :

(i) *Chlorotetracycline* was isolated in 1948 and was introduced under the trade name *Aureomycin.*

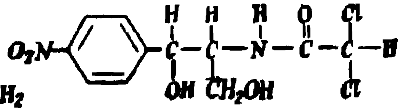
(ii) *Oxytetracycline* was given the trade name *Terramycin.*



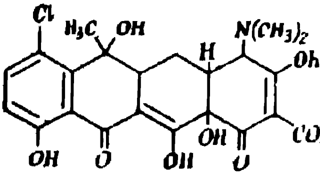
Streptomycin



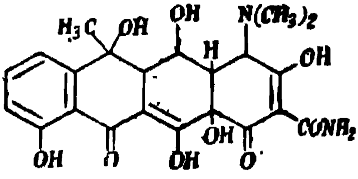
Tetracycline



Chloramphenicol
(Chloromycetin)



Chlorotetracycline
(Aureomycin)



Oxytetracycline
(Terramycin)

Fig. 55·3—Structures of some common antibiotics.

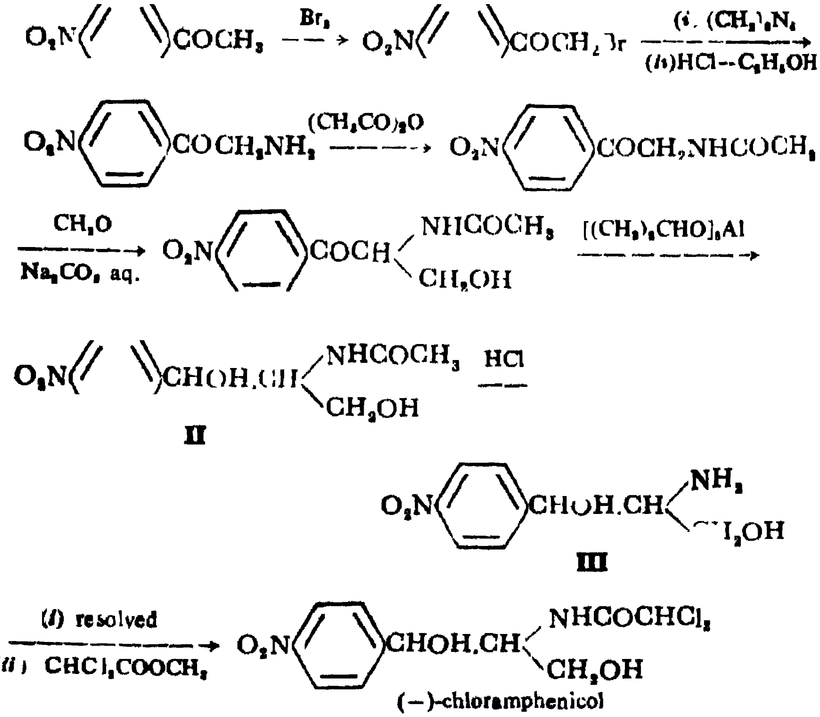
Tetracyclines are broad-spectrum antibiotics and are effective against a number of types of bacteria, larger viruses, protozoa, parasites and also rickettsiae (typhus fever). Unlike penicillin and streptomycin, these can be given orally since they are absorbed from the gastrointestinal tract. On this account they have largely replaced streptomycin.

(*c*) **Chloramphenicol** having the trade name Chloromycetin is effective against typhoid and paratyphoid fevers, diarrhoea and dysentery.

It is also specific for influenza, menengitis, pneumonia, whooping cough and urinary tract infection.

Mode of action. Chloramphenicol interferes with protein synthesis inhibiting the transfer of amino acids from RNA to ribosomes.

Synthesis. Chloramphenicol can be synthesised as follows:



Reduction of compound I gives mainly the *threo*-compound II with a small quantity of the *erythro*-isomer. The mixture is separated by fractional crystallisation Threo-racemate (III) obtained on hydrolysis of II is resolved with the help of (+)-camphorsulphonic acid and D-threo isomer (III) is used for the synthesis of (−)-chloramphenicol.

With passage of time, bacteria become resistant to a certain antibiotic, so we need a stronger antibiotic to destroy these resistant strains. In fact a never-ending race is going on in nature. Nature evolves new bacterial strains which are resistant to antibiotics, while man produces more effective antibiotics to destroy these new more resistant infective bacterial strains.

Antibiotics should not be used indiscriminately since patients may be sensitive to a certain antibiotic and develop allergy immediately or he may get sensitized by its prolonged use.

Mode of Action of Antibiotics. It is believed that antibiotics discourage the growth of bacteria by interfering with the biosynthesis of essential components needed for construction of bacterial cell wall. For example, penicillin inhibits the enzyme, *transpeptidase* which catalyses the final step in the bacterial cell-wall biosynthesis, *viz.*, the cross-linking reaction.

CHEMOTHERAPY IN MALARIA

5. **Malaria.**—It is a fabrile disease caused by protozoa of genus *Plasmodium* (*malaria parasite*) which are transmitted to man by the bites of female mosquitoes of the genus *Anopheles*. There are four types of malaria :

	Protozoa	*Malaria caused*
(i)	Protozoun vivax	Malaria vivax which causes fever on alternate days (*quotidin*).
(ii)	Protozoun malariae	Malaria malariae which causes fever once in three days (*tertian*).
(iii)	Protozoun ovale	Malaria ovale which causes fever once in three days (*tertian*).
(iv)	Protozoun falciparum	Malaria falciparum which causes fever once in four days (*quarton*).

Life Cycle of Malarial Parasite. The chemotherapy of malaria is intimately connected with different stages in the cycle of malarial parasite given below :

(i) *Pre-erythrocytic stage* (*Tissue phase*). The mosquito injects the parasite into the blood of a human being, it immediately goes to the liver cells where it multiplies.

(ii) *Erythrocytic stage*. Once the parasites have grown in adequate number, these come to blood and enter the red blood corpuscles (*erythrocites*). Here again they multiply within the red cells. Eventually the red cells burst liberating the parasites as well as toxins. These toxins cause fever, chills and rigour. The liberated parasites attack fresh red cells and the cycle continues. Depending upon the periodicity of this cycle in the red cells fever comes on alternate days, once in three days or once in four days. Some of the liberated parasites go back to liver and continue the cycle there.

(iii) *Sexual stage*. During the red cycle some of the parasites get converted into male and female gametocytes. These are harmless to human beings but may be taken by a mosquito during a bite to continue the cycle in mosquito to produce the sporozoites which when injected into a human being by a mosquito bite starts the malarial cycle.

6. **Types of Malaria Therapy.**—Choice of an antimalarial drug depends upon the point of its action on the life cycle of the malarial parasite. Various drugs used are :

(*a*) *Casual prophylactic drugs*. These drugs destroy the early tissue forms (sporozoites) in the liver and thereby prevent the erythrocytic stage. Drug commonly used in this stage is Primaquin. Since it is too toxic, its long-term use alone is not advisable.

(*b*) *Suppressive drugs*. These drugs kill the parasites in the blood and do not permit the cycle to continue, thus avoiding the clinical attack. Parasites continue being present in the liver but since red cell cycle is discontinued, the patient does not suffer from fever. The choice drugs for this are proguanil, pyrimethamine and chloroquin.

(*c*) *Drugs used in acute attack*. The suppressive drugs mentioned above when used in higher doses destroy the erythrocytic phase causing relief of symptoms.

(*d*) *Drugs used in radical treatment*. These are the drugs which destroy the persistent tissue phase and the gametocytes. The drug of choice for this purpose is primaquine.

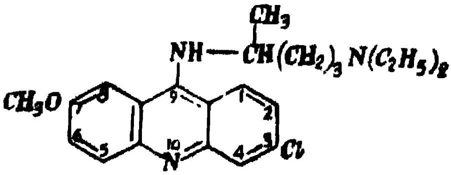
7. **Antimalarial Drugs.**—In earlier days malaria was treated with bark of a tree called cinchona. Later on alkaloid quinine was extracted from cinchona bark and its chloride or sulphate was used as a specific for treatment of malaria for a long time. Quinine has now almost been replaced by more effective synthetic drugs. It is, however, still being used for the treatment of cerebral malaria and in cases resistant to chloroquin. For structure of quinine see page 3·171.

SYNTHETIC DRUGS

Based on their structure, various antimalarial drugs can be classified as follows :

(*a*) **9-Aminoacridines**. An important drug of this class is **Quinacrine,** 3-chloro-9-(4-diethylamino-3-methylbutylamino)-7-methoxyacridine. Its trade names are **Mepacrine, Atabrine and Chinocrine.**

Its structure is as shown below :



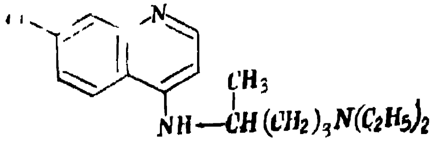
Quinacrine

It attacks the erythrocytic stage of the life cycle of malarial parasites quickly and effectively but apparently has no action on sporozoites. It is effective against both vivax and falciparum malariae.

(*b*) **Derivatives of 4-Aminoquinoline.**

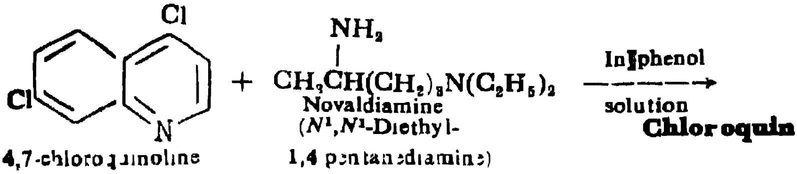
(*i*) **Chloroquine,** *7-Chloro-4-(4-diethylamino-1-methylbutylamino)-quinoline.* Like quinacrine, chloroquine attacks only erythrocytic stage of the life cycle of the malarial parasites. Also it is not effective against gametocides. Consequently, it is not a casual prophylactic or curative drug. As a suppressive drug, however, it is more potent than quinacrine. It does not stain the eyes or skin. It is, therefore, a drug of choice for treatment of malaria. It has been found highly effective in acute attacks of vivax malaria. Relapses can be prevented with weekly doses.

Its structure is as shown below :

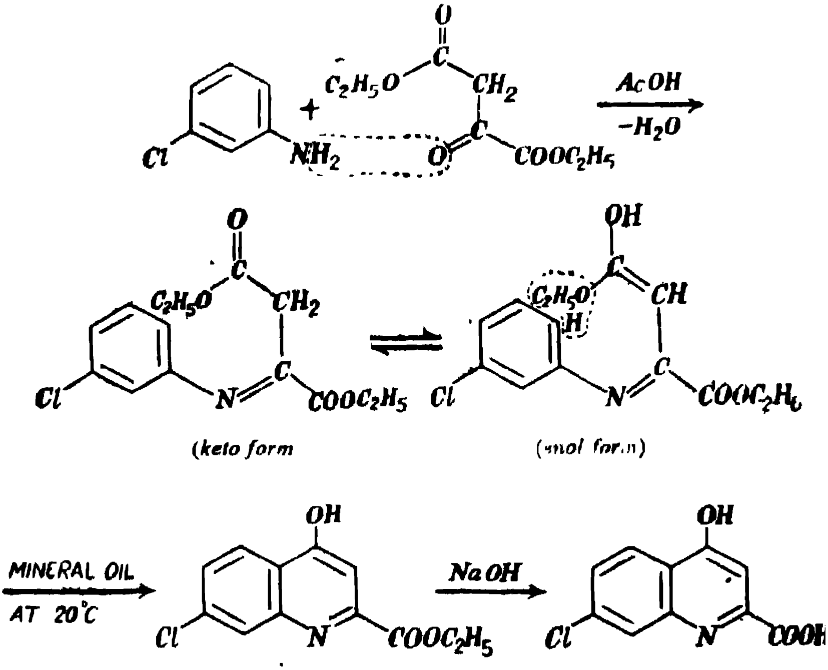


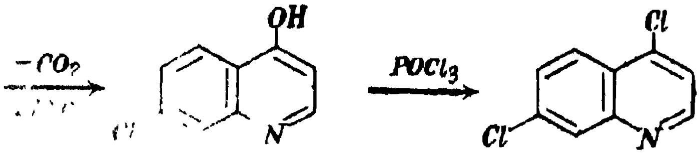
Chloroquine

Synthesis Chloroquine is prepared by heating 4,7-dichloroquinoline with novaldiamine in phenol solution.



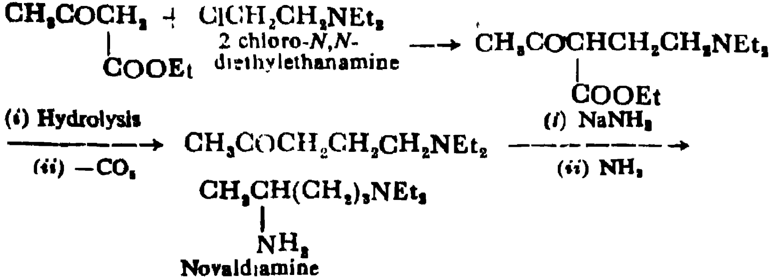
4,7-Dichloroquinoline needed for the purpose is synthesised as follows :





4,7, Dichloroquinoline

Novaldiamine is synthesised from acetoacetic ester as follows :



$$\underset{\displaystyle COOEt}{CH_3COCH_2} + \underset{\text{2 chloro-}N,N\text{-diethylethanamine}}{ClCH_2CH_2NEt_2} \longrightarrow \underset{\displaystyle COOEt}{CH_3COCHCH_2CH_2NEt_2}$$

$$\xrightarrow[\text{(ii) }-CO_2]{\text{(i) Hydrolysis}} CH_3COCH_2CH_2CH_2NEt_2 \xrightarrow[\text{(ii) }NH_3]{\text{(i) }NaNH_2} \underset{\displaystyle NH_2}{CH_3CH(CH_2)_3NEt_2}$$

Novaldiamine

Pharmacological Properties

General. It is absorbed quickly when taken orally. 50% of it gets plasma protein bound. It gets concentrated up to several hundred times in liver, kidney, spleen and eyes but does not act on hepatic cycle.

(*i*) It acts on erythrocytic cycle of plasmodium vivax malariae and ovale. Thus it causes suppressive prophylaxis and suppressive cure. It abolishes acute attack of malaria.

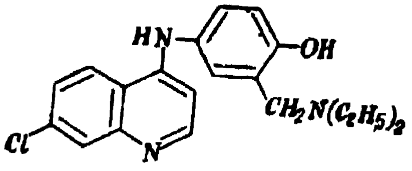
(*ii*) It kills amoeba. It is, therefore, effective in intestinal, hepatic and cutaneous amoebiasis.

(*iii*) It is useful in the following disorders :

Rheumatoid arthritis, Sarcoidosis (fungal disease), Infectious mononucleosis (viral diseases), solar urticaria (छपाकी), Diabetic neuritis (inflammation of nerves).

Mode of Action. It inhibits synthesis of DNA by blocking DNA replication and degrading the ribosomes.

(ii) **Camoquine.** It is another derivative of 4-aminoquinoline. It is less toxic and 3-4 times as active as quinine. It is a highly suppressive drug in vivax malariae and falciparum malaria. Its structure is given below :



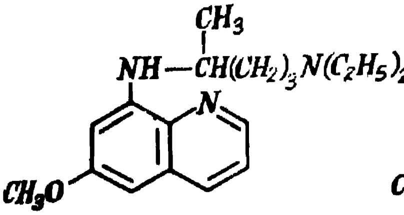
Camoquine

(*c*) **Derivatives of 8-Aminoquinolines.** Some important 8-aminoquinolines are

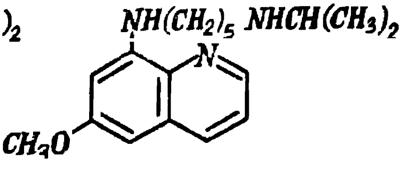
(*i*) **Pamaquine,** (*ii*) **Pentaquine,**

(*iii*) **Isopentaquine,** · and (*iv*) **Primaquin.**

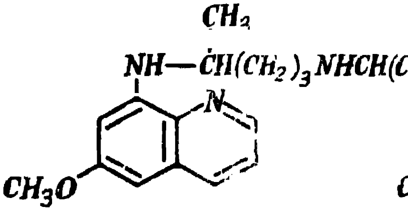
These constitute a group of most promising antimalarial drugs which are highly active against the tissue forms of protozoun vivax and protozoun falciparum. However, these are used only in combination with quinine or some 4-aminoquinoline. Their structures are shown below :



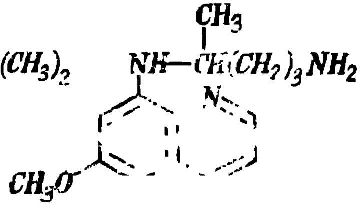
Pamaquine



Pentaquine



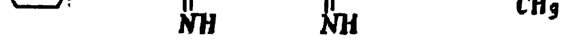
iso-Pentaquine



Primaquine

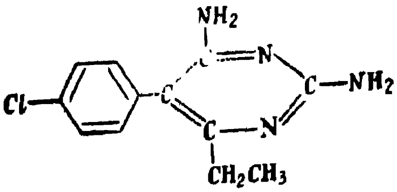
(*d*) **Pyrimidine and Biguanidine Derivatives.** Two important drugs of this group are :

(i) **Proguanil** having trade name **Paludrine.** It is less toxic and does not colour the skin. It is a suppressive drug of choice for both falciparum as well as vivax malariae. Its structure is given below :



Paludrine

(ii) **Pyrimethamine.** It is the most powerful suppressive drug known so far and is, therefore, a drug of choice as suppressive drug as well as the one used in acute attack. Its structure is shown below :



Pyrimethamine

ANTIPYRETICS AND ANALGESICS

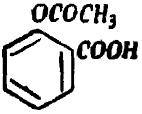
8. **Antipyretics.**— These drugs are used for bringing down the body temperature in high fevers. They act through excessive sweating and thereby cooling the body. Examples of common antipyretics are :

(*i*) Acetylsalicylic acid (aspirin), (*ii*) Analgin,

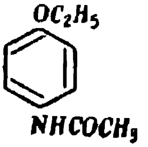
(*iii*) Paracitamol (4-Acetamidophenol), (*iv*) Phenacetin,

(*v*) Phenylbutazone (Butazolidine).

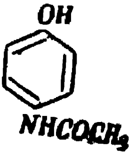
Most of them produce excessive secretion of the acid in the stomach and may cause ulcers. They should not be taken empty stomach. Their excessive use should be discouraged.



Acetylsalicylic acid (*Aspirin*)



Phenacetin



Paracetamol

(1) **Aspirin** (*Acetylsalicylic acid*).

Synthesis. Aspirin is obtained by acetylation of salicylic acid (see page 2·664). Salicylic acid needed for the purpose is prepared by heating solid sodium phenoxide to 390-415K with carbon dioxide under pressure (Kolbe-Schmitt method, see page 2·661).

Uses : (*i*) *As an analygesic* for relief of pain like headache, bodyaches, arthritis (joint pains).

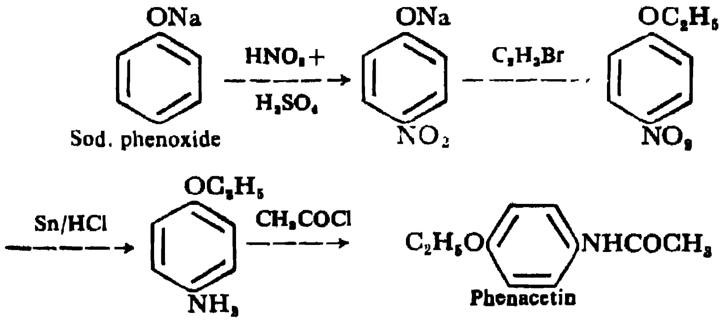
(*ii*) *As an antipyretic* to bring down high temperature (fever) due to all types of diseases.

(*iii*) *As an anti-inflammatory*, to bring down inflammation, *e.g.*, rheumatoid arthritis, spondylitis.

It is used singly or in combination with phenacetin or caffeine.

(2) **Phenacetin** (*p-ethoxyacetanilide*).

Synthesis. It is manufactured as follows :



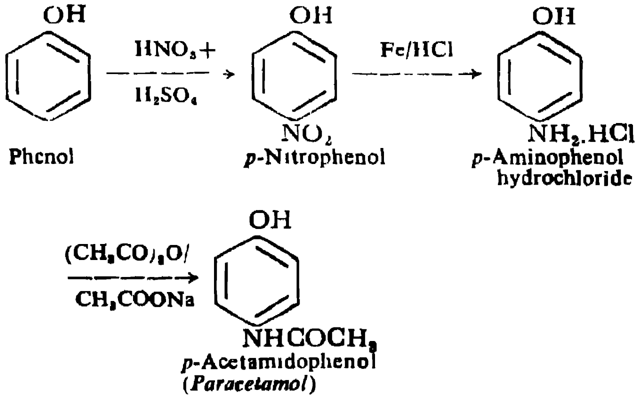
Uses : It is used as (*i*) an antipyretic, (*ii*) an analgesic and

(*ii*) antirhuematic

It is usually used in combination with other drugs.

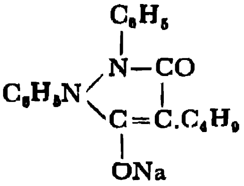
(3) **Paracetamol** (*N-acetyl-p-aminophenol*).

Synthesis.



Uses : (*i*) As an antipyretic (*ii*) As an analgesic

(4) **Phenylbutazone** (trade name *Butazolidine*). It is a pyrazolone derivative with structural formula as given below :



1,2-Diphenyl-4-butyl-3,5-pyrazolinedione (pheylbutazone)

Uses : (*i*) *As an antipyretic* to bring down fever.

(*ii*) *As anti-inflammatory* in arthritic conditions, eye operation

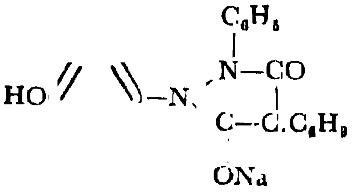
(*iii*) *As an analgesic* in arthritic conditions, gouts.

(*iv*) *As uricosuric* in gout for removal of uric acid.

Due to its high toxicity it is not considered as a very safe drug.

Oxyphenylbutazone (trade name *Tandearil* or *Suganril*) is

1-(*p*-hydroxyphenyl)-2-phenyl-4-butyl-3,5-pyrazolinedione. It is more potent and less toxic than phenylbutazone.



Oxyphenylbutazone
(Tandearil or Suganril)

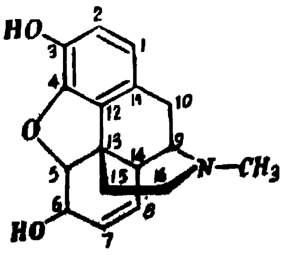
Side Effects of these drugs :

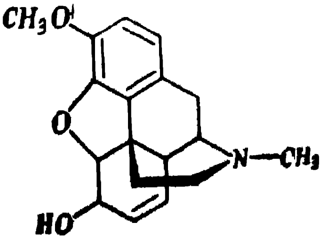
Phenacetin is a weak drug and is commonly used only in combination with aspirin. Aspirin causes intestinal side effects, *e.g.*, it causes gastritis which leads to vomiting, nausea and even bleeding. Paracetamol causes kidney damage. Phenylbutazone is highly toxic and hence not considered a safe drug. It is replaced by oxyphenyl-butazone these days.

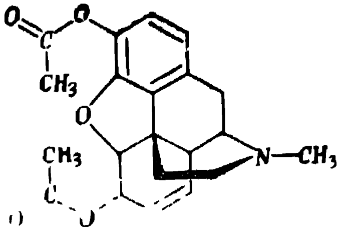
Patients who cannot tolerate aspirin are given paracetamol which is superior to aspirin as an antipyretic. Similarly patients having kidney defects cannot tolerate paracetamol. They are given aspirin which is more potent analgesic than paracetamol.

9. **Analgesics.**—Drugs which relieve or decrease pain are termed analgesics. These are of two types : (i) Narcotics and (ii) Non-narcotics.

(*a*) **Narcotics.** These are mainly opium and its products, *e.g.*, morphine, codeine and heroin. They cause addiction. This group of drugs is more effective in their analgesic properties. They also cause sleep and unconsciousness in higher doses.

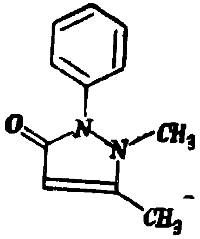






Heroin

(b) **Non-narcotics**. This group of drugs also have antipyretic properties. Common drugs are aspirin and analgin.



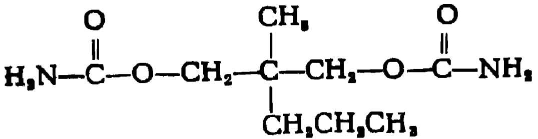
Analgin

(2, 3-Dimethyl-1-phenyl-3-pyrazonolin-5-one)

TRANQUILLIZERS, HYPNOTICS AND PSYCHEDELIC DRUGS

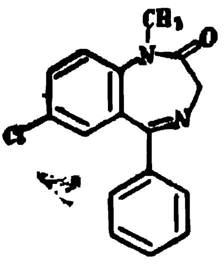
10. **Tranquillizers**.—These reduce anxiety and tension. They are basically of two types :

(a) **Sedatives**. These are used for patients who are violent or mentally agitated. The common drugs used are : meprobamate (equanil), diazepam (calmpose).



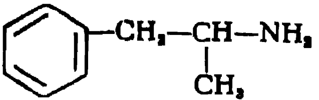
$$H_2N-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2-\underset{\underset{\displaystyle CH_2CH_2CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_2-O-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2$$

Equanil

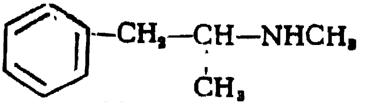


Diazepam (Calmpose)

(*b*) **Antidepressants, Mood Elevators or Pep Pills.** Sometimes the patients are highly depressed and lose self-confidence. In the case of such patients antidepressants are given. These drugs produce feeling of well-being and improve efficiency. Some axamples of antidepressants are : tofranil, vitalin, amphetamines and cocaine.

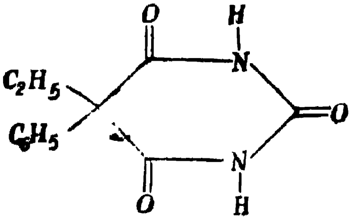


Amphetamine
(Benzedrine)

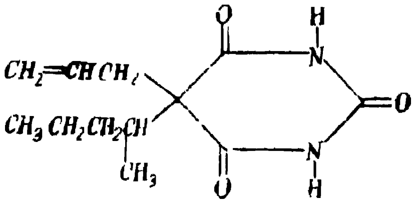


Methamphetamine
(Methedrine)

11. **Hypnotics.**—These drugs produce sleep and are habit forming. Common examples of hypnotics are luminal, seconal and sonryl. These are also used as sedative tranquillizers.

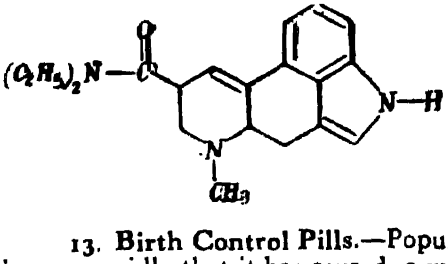


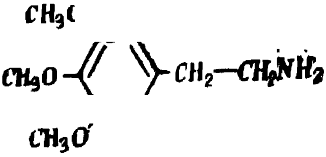
Luminal
(Phenobarbital)



Seconal
(Secobarbital)

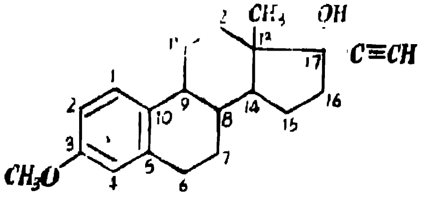
12. **Psychedelic Drugs.**—These drugs produce visual and auditory hallucinations. The person after taking the drugs sees objects and hears sounds which do not exist. They produce euphoria —a sense of well-being, overjoy, self-confidence, etc. But these drugs are harmful to the body and addiction occurs in a very short period. Common drugs are : lysergic acid diethvlamide (LSD-25) and mescaline (3, 4, 5-trimethoxyphenyl-ethylamine),



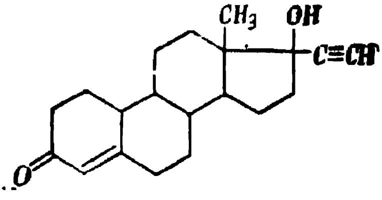


13. **Birth Control Pills.**—Population of the world is growing so rapidly that it has caused a worldwide concern. Various techniques to control birth rate are being used. In recent years, drugs have been developed that control ovulation and, if regularly taken, function as extremely effective contraceptives. Thus women, using these pills at regular intervals, do not conceive and produce children. These drugs thus function as extremely effective contraceptives. The invention of these pills has basically altered the techniques of birth control and will have a world-wide impact on society.

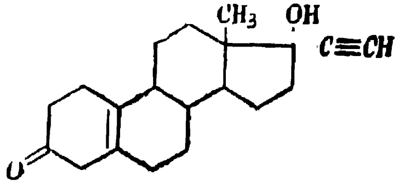
Two successful drugs used as birth control pills are *Orthonovum* and ***Enovid***. Both of these are combination of drugs.



MESTRANOL



NORETHINDRONE



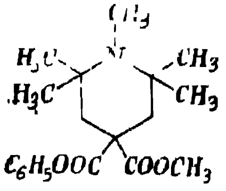
NORETHYNODREL

For example, orthonovum is a mixture of norethindrone (17 α-ethynyl-19-nortestosterone) and mestranol (17-α ethynyl-3-methoxy-1, 3, 5 (10)-estratrien-17-β-ol]. Similarly, enovid is a mixture of norethynodrel [17-α-ethynyl-17-β hydroxy-5 (10)-estern-3-one] and mestranol.

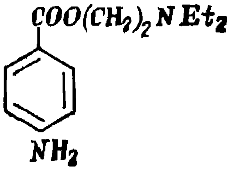
ANAESTHETICS

14. **Anaesthetics.**—These produce loss of sensation. Anaesthetics are of two types ·

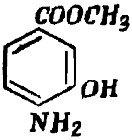
(*a*) **Local anaesthetics** which produce loss of sensation on a small area where the drug is applied. Common local anaesthetics are : xylocaine (used in jelly form), ethyl chloride (used in spray form) and procaine (used in injection) Local anaesthetics are used for small surgical operations like tooth extraction, stitching of a wound or incision of an abscess. Some other modern local anaesthetics are ; α-Eucaine, orthoform and dimethisquin.



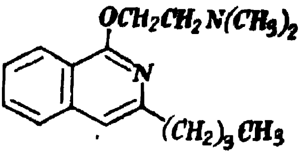
α-Eucaine



Procaine



Orthoform



Dimethisquin

(*b*) **General Anaesthetics.** They produce unconsciousness and are used for major surgical operations. These may be used in the form of gas, *e.g.*, nitrous oxide, cyclopropane or may be given in the injection form, *e.g.*, sodium pentothal. Ether and chloroform used as general anaesthetics previously have been discarded in favour of better ones available now.

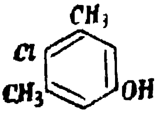
ANTISEPTICS AND DISINFECTANTS

15. **Chemicals used for Sterilisation.**—Various chemicals used for sterilisation are classified under two headings : (i) Antiseptics and (ii) Disinfectants

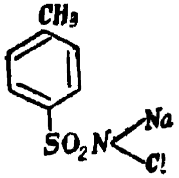
(*a*) **Antiseptics.** An antiseptic may kill the bacteria or may only prevent its multiplication. They do not harm the living tissues and can be applied on cuts and wounds. Some common examples of antiseptics are · dettol, cetavelon, savlon, acriflavin, gentian violet, mercurochrome (*see page* 3·285), boric acid and potassium permanganate.

(*b*) **Disinfectants.** They kill the bacteria and are used for sterilization of inanimate objects like instruments, utensils, clothes, floors, sanitary fittings, sputum and excreta. They are harmful to the living tissues and cannot be used on the skin. Some examples of disinfectants are : phenol, methylphenol, hydrogen peroxide and sulphur dioxide.

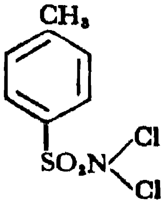
Some of these compounds are shown below :



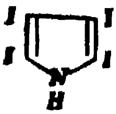
Dettol



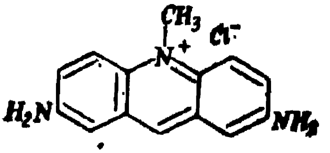
Chloramine-T



Dichloramine-T



Iodol



Acriflavin

Depending upon the concentration, the same substance may be used as an antiseptic or disinfectant. In smaller concentrations it is an antiseptic whereas in higher concentrations it becomes disinfectant. For example, 0·2% solution of phenol is an antiseptic while 1·0% solution of phenol is disinfectant.

Germicide and fungicide are general terms used for substances which destroy or kill germs and fungi respectively.

The mode of action of these chemicals is :

(*a*) *As oxidising agents*, *e.g.*, potassium permanganate, hydrogen peroxide, bleaching powder, tincture of iodine and chlorine used for sterilization of water.

(*d*) *As metabolic poisons*, *e.g.*, mercurochrome, acriflavin, silver nitrate and formaldehyde.

PESTICIDES

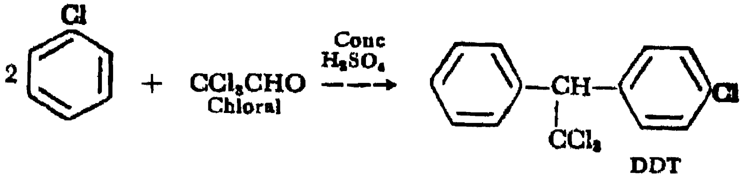
16. **Pesticides.**—Insects, fungi and weeds are most serious problems of the farmer. They destroy standing crops and stored foodgrains. One of the factors which has helped progress in agriculture has been our ability to control insect pests and weeds.

In this section we shall deal with various chemicals called pesticides which have proved effective against insects (insecticides), fungi (fungicides) and weeds (herbicides).

These are all poisons and must be used with utmost care. Their indiscriminate use could lead to pollution of streams with all fish killed, annihilation of birds, human sickness and in some cases even death.

(*a*) **Insecticides.** Commonly used insecticides are :

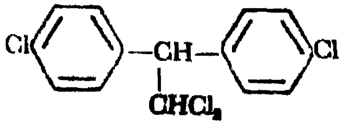
(*i*) **DDT**, 2,2-bis-(4-chlorophenyl)-1,1,1-trichloroethane, also known as *p,p*'-dichlorodipheyltrichloroethane (hence DDT), is synthesized by the condensation of 1 mole of chloral with 2 moles of monochlorobenzene in the presence of sulphuric acid



It is practically insoluble in water, moderately soluble in hydroxylic and polar solvents and in petroleum oils. It is readily soluble in most aromatic and chlorinated solvents.

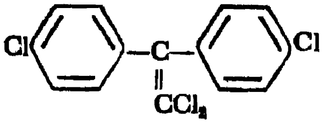
Two other similar chlorinated hydrocarbons are DDD and DDE.

DDD. It is 2,2-*bis*-(4-chlorophenyl)-1,1-dichloroethane, also known as *p*, *p*'-dichlorodiphenyldichloroethane, hence DDD.

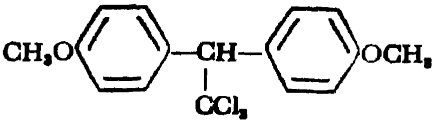


For its synthesis, ethanol is chlorinated below 310K until the lower layer has a density 1·29. This is condensed with monochlorobenzene.

DDE is 2,2-*bis*-(4-chlorophenyl)-1,1-dichloroethene.

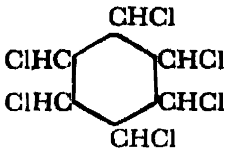


(*ii*) **Methoxychlore** or 2,2-*bis*-(3-methoxyphenyl)-1,1,1- trichloroethane,



It is obtained by condensation of chloral and methoxybenzene. It is a grey flaky powder practically insoluble in water, moderately soluble in ethanol and petroleum oils. However, it is readily soluble in most aromatic solvents.

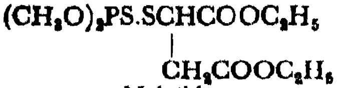
(*iii*) **Benzene hexachloride** (**BHC**). It is marketed under the trade name Gammexane or 666. Chemically it is the γ-isomer of 1, 2, 3, 4, 5, 6-haxachlorocyclohexane. Gammexane contains only about 15% of the γ-isomer. Preparation containing about 99% γ-isomer is named **Lindane**.



BHC is prepared by the chlorination of benzene under ultraviolet light. It is an off-white to brown powder of persistent musty odour. It is practically insoluble in water, soluble in benzene and chloroform.

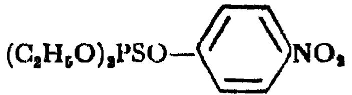
Use of these insecticides over long periods has resulted in development of resistance in various insects. Due to their accumulation in the animal bodies, birds and fish had malfunctioning of their bodies and quite a number of them died as a result of it. Moreover, insecticides destroy both harmful as well as useful insects.

(*iv*) **Organo-phosphates.** Some of the organo-phosphates used as insecticides are *malathion* and *parathion*.



$$\begin{array}{l}(CH_3O)_2PS.SCHCOOC_2H_5\\ \qquad\qquad\;\;|\\ \qquad\quad CH_2COOC_2H_5\end{array}$$

Malathion



Parathion

These are relatively safer inseticides but highly toxic to man and animals. Their advantage is in their being less persistent due to easier degradation but this requires application more often.

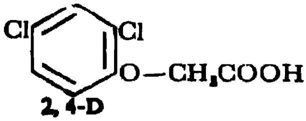
Malathion is prepared by the addition of *OO*-dimethyl phosphorodithioic acid to diethyl malate, hydroquinone being present to suppress the polymerisation of the unsaturated ester. Its solubility in water is 145 ppm. It is miscible with many organic solvents.

Parathion is made by condensation of diethyl phosphorochloridothionate with sodium *p*-nitrophenate. It is a pale yellow liquid and its solubility in water at room temperature is 24 ppm. It is miscible with most organic solvents.

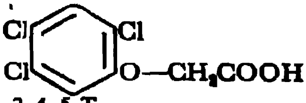
A more recent method for insect control is the use of hormones which upset the growth cycle in insects.

(*b*) **Herbicides.** Virtually every crop and ornamental plant has a weed problem. Weeds take away a good part of the fertilizer and water needed by the plants. Control of weeds has, therefore, become a challenge to efficient farming. Herbicides are chemicals used for destroying weeds. Some common herbicides are

(*i*) 2, 4 dichlorophenoxyacetic acid (2, 4-D),
(*ii*) 2,4,5-trichlorophenoxyacetic acid (2,4 5-T) and (*iii*) diuron.



2, 4-D



2, 4, 5-T

(*c*) **Fungicides.** Some common fungicides are copper sulphate, copper naphthenate, 2, 4, 6-trichlorophenol and some compounds of mercury. Bordeaux mixture used as fungicide is a mixture of $CuSO_4$, lime and water. Dithiocarbamates are the most important organic fungicides.

(*d*) **Rodenticides.** In addition to these pests, rats are a big nuisance to the farmer. They destroy food stocks and spread diseases. Some chemicals used for killing rats are sodium monochloroacetate, zinc phosphide, sodium fluoroacetate and thalium sulphate. These are mixed with food and kept for the rats to eat and die. Alpha-naphthylthiourea (ANTU) can also be used for the purpose.

Mode of Action of Pesticides. Little is known as yet about the exact mechanism by which pesticides exert their selectively lethal effect. Probably these function as poisons for the important biological process of insects, fungi and herbs. Interruption of these biological processes leads to death of the organism.

QUESTIONS

Essay Type :

1. How are diseases caused ? How can these be prevented ? What is chemotherapy ?

2. What do you know about the chance discovery of sulphanilamide ?

3. What are sulpha drugs ? Write names and formulae of any three sulpha drugs you are familiar with. Give the preparation of one of these. Discuss the mode of action of sulpha drugs.

4. Write a note on active-site concept of enzymatic catalysis. Discuss its utility in explaining the mode of action of sulpha drugs.

5. What is an antibiotic ? What do you know about the chance discovery of penicillin ? Give the general formula for various penicillins and write the formula of penicillin G.

6. Name three antibiotics other than penicillin and write structural formula for one of these. In what respect these may be considered superior to penicillin ? What precautions are necessary in the use of antibiotics ? What is their mode of action ?

7. What is malaria ? How are different types of malaria caused ? What do you know about the life cycle of malarial parasite ?

8. Discuss different types of malaria therapy.

9. What are the different types of antimalarial drugs ? Give examples of each type.

10. Write short notes on any three of the following :

(i) Antipyretics, (ii) Analgesics,
(iii) Tranquillizers, (iv) Hypnotics, and
(v) Psychedelic drugs.

11. What are anaesthetics ? Name three modern local anaesthetics and write their formulae.

12. What do you understand by antiseptics and disinfectants ? Give three examples of each. What is the mode of action of these chemicals ?

13. Write a short note on birth control pills.

14. What are pesticides ? How are these classified ? Give two examples of each class of pesticides.

Short Answer Type :

1. Define chemotherapy.

2. How are prontosil and sulphanilamide related to each other ?

3. What are sulpha drugs ?

4. Which sulpha drugs are specific cure for the following diseases :

(i) Pneumonia, (ii) Urinary tract infections,
(iii) Gastrointestinal tract infections.

5. What is the mode of action of sulpha drugs ?

6. What is active-site concept of enzymatic catalysis ?

7. Name the compound which acts as inhibitor in the enzymatic steps involved in the synthesis of folic acid from *p*-aminobenzoic acid.

8. Name a drug which has proved effective in the treatment of cancer.

9. What are antibiotics ?

10. Give the general formula for penicillins. Name the antibiotics which can cure the following diseases:
(i) Tuberculosis, (ii) Typhoid.

11. Why penicillin cannot be administered orally ?

12. What are the drawbacks of penicillin as antibiotic ?

13. Why antibiotics should not be used indiscriminately ?

14. What is the mode of action of antibiotics ?

15. Give the synthesis of (–)-Chloroamphenicol. For what purpose is it used ? (*Delhi B.Sc. Hons. 1982*)

16. What is malaria ?

17. Where are malarial parasites present in the following stages :

(i) Pre-erythrocytic stage. (ii) Erythrocytic stage. (iii) Sexual stage.

18. (*a*) What is the function of casual prophylactic drugs in malaria therapy ?

(*b*) What is the function of suppressive drugs in malaria therapy ? Name three suppressive drugs of choice.

19. What is the function of drugs used in radical treatment of malaria ? Name one drug used for the purpose.

20. Name one antimalarial drug for each one of the following types :

(*a*) 9-Aminoacridines. (*b*) 4-Aminoquinolines. (*c*) 8-Aminoquinolines.

(*d*) Derivatives of Pyrimidine and Biguanidine.

21. (*a*) What are the main pharmocological properties of chloroquin ? (*Delhi B.Sc. Hons. 1982*)

(*b*) Give the synthsis of chloroquin. (*Delhi B Sc 1982*)

22. (*a*) What are antipyretics ? Can antipyretics be analgesics ? If yes, give an example.

(*b*) What are different types of analgesics ? Give examples.

23. How can paracetamol be prepared ? Why is this drug widely used as a useful alternative analgesic to aspirin and phenacetin ? (*Delhi B.Sc. Hons. 1982*)

24. Write the structure of phenylbutazone and give the synthesis of phenacetine. Give the uses of aspirin. (*Delhi B.Sc. 1982*)

25. (*a*) What are different types of Trânquillizers ? Give examples.

(*b*) What are hypnotics ? Give one example.

26. What are Psychedelic drugs ? Give two examples.

27. What is a local anaesthetic ? Give one example.

28. What are antiseptics ? Give two examples.

29. What are disinfectants ? Give two examples.

30. What is the difference between an antiseptic and a disinfectant ?

31. What is the mode of action of antiseptics and disinfectants ?

32. What is the function of a birth control pill ?

33. Name two drugs used as birth control pills. Give the composition of each.

34. Name the action of the following drugs :

(*a*) Aspirin, (*b*) Penicillin, (*c*) Phenacetin,
(*d*) Morphine, (*e*) Analgin, (*f*) Meprobamate,
(*g*) Tofranil, (*h*) Luminal, (i) LSD.

35. What is the difference between a pep pill and birth control pill ?

36. What are plant pesticides ? Which different types of pesticides you are familiar with ?

37. What are the following ? Give two examples of each

(*a*) Insecticides, (b) Herbicides, (c) Fungicides and (*d*) Rodenticides.

38. How is DDT prepared on a large scale ? (*Delhi B.Sc. 1982*)

12

Polymers

1. **Polymerisation.**—When ethylene is heated under pressure with oxygen, the product is essentially an alkane with a very long chain and very high molecular weight. It is made up of many ethylene units and is, therefore, called *polyethylene* (*poly*=many)—a familiar plastic material used in making polythene bags.

***Joining of small molecules to make very large or macro molecules is termed* polymerisation.** The compound composed of these very large number of molecules is called a **polymer** (Greek : *poly*+ *meros*=many parts). The simple compounds from which polymers are made are called **monomers.**

$$\underset{\substack{\text{Ethylene}\\ \text{(monomers)}}}{n\ CH_2{=}CH_2} \xrightarrow[\text{pressure}]{O_2,\ \text{heat}} \ldots CH_2-CH_2-CH_2-CH_2-CH_2-CH_2 \ldots$$

$$\text{or } \underset{\substack{\text{Polyethylene}\\ \text{(a polymer)}}}{(-CH_2-CH_2-)_n}$$

Two monomer units combine to give a *dimer*. Three such units combine to form a *trimer*. Similarly, a *tetramer* is made up of four monomer units whereas a pentamer is made up of five such units.

Monomer	A
Dimer	A—A
Trimer	A—A—A
Tetramer	A—A—A—A
Pentamer	A—A—A—A—A

2. **Copolymerisation.**—A polymer obtained from any pure monomer A, is a homopolymer, poly A.

—A—A—A—A—A—A—

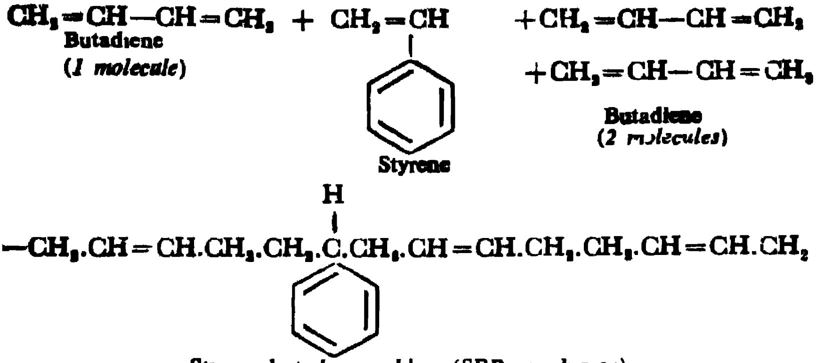
Similarly, another monomer B on polymerisation gives another homopolymer, poly B.

—B—B—B—B—B—

If, however, we start with a mixture of two monomers A and B, this on polymerisation gives a polymer containing both the monomers A and B such as

—A—B— A—B—
—A—B—B—A—B—B—

Such a polymer is called *copolymer.* In a copolymer, there is a nearly perfect alternation of monomer units and its properties are determined by the ratio of A to B. Its properties are different from and often superior to those of poly A and poly B. For example, synthetic rubber obtained by polymerisation of styrene is found to be hard thermoplastic with little elasticity and the one obtained by polymerisation of butadiene is equally unserviceable. However, a 1-to-3 copolymer of styrene and butadiene has been found to be a very useful product possessing properties very much like those of natural rubber.



Styrene-butadiene rubber (SBR copolymer)

3. **Importance of Polymers.**—Polymers are today one of the most important products which surround us in every walk of life. Proteins and carbohydrates are natural polymers and are important constituents of our food. Synthetic fibres, resins, plastics, natural rubber and synthetic rubber—the blessings of modern researches in chemistry, are all polymers. These play an extremely important role in our daily life By use of plastics blind persons can be made to see and cripples enabled to walk. Internal damaged organs like heart valves can be repaired and some like trachea and ureter even replaced.

4. **Types of Polymers.**—On the basis of their structure, polymers are of three types ·

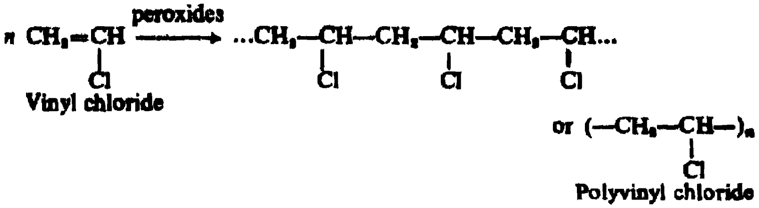
(*a*) **Linear Polymers.** These consist of extremely long chains of atoms. These chains may be slightly branched but are not linked laterally to other chains. These may also be termed one-dimensional polymers. Examples of linear polymers are polyethylene and polyvinyl chloride.

(*b*) **Network or Sheet Polymers.** Those polymers in which long chains of atoms are linked laterally to other similar chains to form networks are termed network or sheet polymers. Their molecules are essentially two dimensional having great length and breadth but not very thick.

(*c*) **Three dimensional Polymers.** Those polymers in which chains are cross-linked to give a three-dimensional network solid are termed three dimensional polymers. Bakelite (phenol-formaldehyde resin) is a common example of this type.

5. Types of Polymerisation Reactions.- -Polymerisation is of two types :

(*a*) **Chain reaction Polymerisation or Addition Polymerisation.** *It involves a series of reactions each of which consumes a reactive particle and produces another similar one. The reactive particles may be free radicals, cations or anions.* Polymerisation of ethylene given realier is an example *of addition polymerisation.* It is an important reaction of alkenes and conjugated dienes—and indeed of all kinds of compounds that contain carbon-carbon double bonds. For example, vinyl chloride polymerises to yield *polyvinyl chloride* in which chlorine atoms are attached at regular intervals.



$$n\,CH_2{=}\underset{Cl}{\underset{|}{CH}} \xrightarrow{\text{peroxides}} \ldots CH_2{-}\underset{Cl}{\underset{|}{CH}}{-}CH_2{-}\underset{Cl}{\underset{|}{CH}}{-}CH_2{-}\underset{Cl}{\underset{|}{CH}}\ldots$$

Vinyl chloride

$$\text{or } (-CH_2{-}\underset{Cl}{\underset{|}{CH}}-)_n$$

Polyvinyl chloride

Polyvinyl chloride is termed an **addition polymer**. It is used in making phonograph records, plastic pipes. It is plasticized with high-boiling esters for making raincoats, metal coatings and upholstery fabrics.

Some common addition polymers have been listed in Table 12·1.

Table 12·1—Some Common Addition Polymers

Repeating unit (Monomer)	Polymer (Common Name)	Uses
$CH_2{=}CHCl$ Vinyl chloride	Polyvinyl chloride (PVC)	PVC sheets, water pipes, hoses, handbags
$CH_2{=}CH_2$ Ethylene	Polyethylene	Coats, wire insulators, bags
$CH_2{=}\underset{C_6H_5}{\underset{\lvert}{CH}}$ Vinylbenzene —Styrene)	Polystyrene	Combs
$CH_2{=}\underset{OOCCH_3}{\underset{\lvert}{CH}}$ Vinyl acetate	Polyvinyl acetate	Latex paint
$CH_2{=}CH{-}CN$ Acrylonitrile	Polyacrylonitrile (PAN)	Rug fibres
$CH_2{=}CH{-}CH{=}CH_2$ 1, 3-Butadiene	BUNA rubbers	Tyres and hoses
$CF_2{=}CF_2$ Tetrafluoroethylene	Polytetrafluoro-ethylene (Teflon)	Insulators and bearings

There are three possible ways in which addition polymerisation can occur :

(*i*) ***Head to Tail*** :

$$-\underset{H}{CH_2}-\underset{T}{CHY}-\underset{H}{CH_2}-\underset{T}{CHY}-\underset{H}{CH_2}-\underset{T}{CHY}$$

(*ii*) ***Head to head to Tail to tail*** :

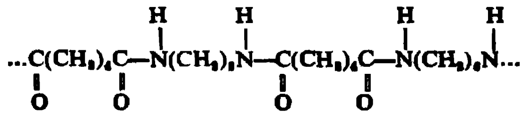
$$-\underset{T}{CHY}-\underset{H}{CH_2}\ -\underset{H}{CH_2}-\underset{T}{CHY}-\underset{T}{CHY}-\underset{H}{CH_2}-\underset{H}{CH_2}-\underset{T}{CHY}-$$

(*iii*) ***A random arrangement involving both*** (*i*) ***and*** (*ii*).

Experimental evidence shows that head to tail union is the most favoured in polymerisation reactions.

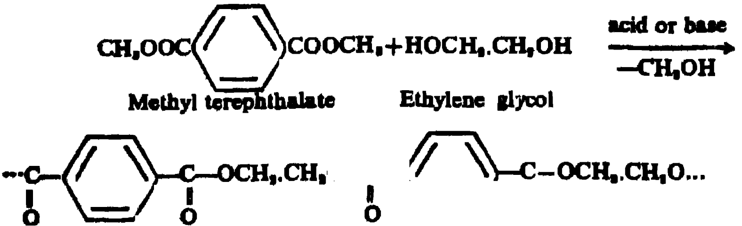
(*b*) **Step-reaction Polymerisation or Condensation Polymerisation.** ***It involves a series of reactions each of which is essentially independent of the preceding one. Formation of polymer is possible simply because monomer happens to undergo reaction at more than one functional group.*** Carboxylic acids react with amines to form amides and with alcohols to form esters. When an acid that contains more than one —COOH group reacts with an amine that contains more than one —NH_2 group, or with an alcohol that contains more than one —OH group, then the products are polyamides and polyesters. For example :

$$\underset{\text{Adipic acid}}{HOOC.(CH_2)_4.COOH} + \underset{\text{Hexamethylene-diamine}}{H_2N(CH_2)_6NH_2} \longrightarrow \text{Salt}\ \xrightarrow[-H_2O]{\text{Heat}}$$



$$\ldots\underset{\underset{O}{\|}}{C}(CH_2)_4\underset{\underset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}(CH_2)_6\overset{\overset{H}{|}}{N}-\underset{\underset{O}{\|}}{C}(CH_2)_4\underset{\underset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}(CH_2)_6\overset{\overset{H}{|}}{N}\ldots$$

Nylon 66 (*A polyamide*)



Terylene or Decron (*A polyester*)

These are examples of condensation polymerisation since monomer molecules are combined with the loss of simple molecules, *e.g.*, water, methanol (as in above cases), etc.

These polymers are termed **condensation polymers** and are used in the manufacture of synthetic fibres and threads.

Some common condensation polymers have been given in **Table 12·2.**

Table 12·2—Some Common Condensation Polymers

Monomer	Molecule Eliminated	Polymer	Uses
1. Hexamethylene-diamine+adipic acid	H_2O	Nylon 66	Hosiery, fabrics, ropes
2. Ethylene glycol +dimethyl terephthalate	CH_3OH	Terylene or Dacron	Fabrics
3. Maleic anhydride +Methylene glycol	H_2O	Alkyl plastic	Adhesives, cements, floor finishes
4. Formaldehyde +Urea	H_2O	Urea-formaldehyde resin	Adhesives, toys, buttons
5. Ethylene glycol+ ethylene diisocyanate	H_2O	Polyurethane	Paints, fibres, heat insulation

6. Mechanism of Chain-reaction Polymerisation.—Polymerisation, say of a vinyl monomer, proceeds in the presence of a variety of reagents termed *initiators. These are used up during the reaction hence cannot be termed catalysts*. An initiator initiates a reaction by forming some reactive species, such as an ion or a free radical which can add to a double bond forming a new ion or a radical. The new ion or radical can, in turn, add to another monomer and thus a chain reaction starts. Depending upon the chemical nature of the growing polymer chain, polymerisation is of two types :

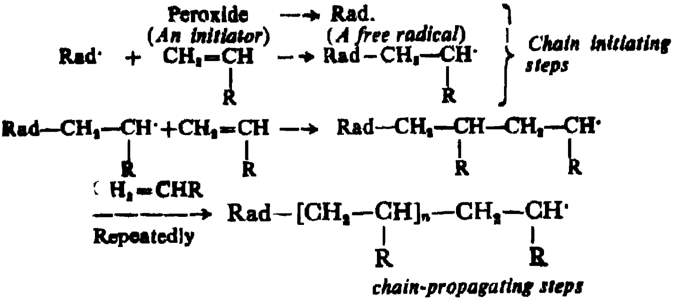
(*a*) *Free Radical Polymerisation*. These are polymerisation reactions started by initiators which produce reactive free radicals at a controllable rate.

(*b*) *Ionic Polymerisation*. These are the polymerisation reactions brought about by initiators which produce ions responsible for the chain reaction. The ion produced may be a carbocation, R^+ (a cation) or a carbanion : R^- (an anion). Depending upon the nature of the ion, therefore, ionic polymerisation is of two types :

(*i*) *Cationic polymerisation*. It is a chain reaction propagated by cations (positively charged ions).

(*ii*) *Anionic polymerisation*. In this the chain reaction leading to polymerisation is propagated by anions (negatively charged ions).

7. Free-radical Polymerisation of Alkenes and Dienes.—During polymerisation of alkenes the presence of a small amount of an initiator is necessary. Commonly known initiators are peroxides and the polymerisation proceeds via a free-radical mechanism in the following steps :



$$\underset{\text{(An initiator)}}{\text{Peroxide}} \longrightarrow \underset{\text{(A free radical)}}{\text{Rad.}}$$

$$\text{Rad}^{\cdot} + CH_2=\underset{R}{CH} \longrightarrow \text{Rad}-CH_2-\underset{R}{CH}^{\cdot}$$

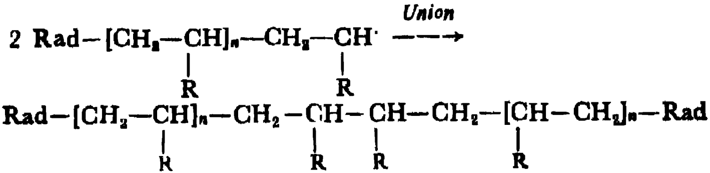
Chain initiating steps

$$\text{Rad}-CH_2-\underset{R}{CH}^{\cdot}+CH_2=\underset{R}{CH} \longrightarrow \text{Rad}-CH_2-\underset{R}{CH}-CH_2-\underset{R}{CH}^{\cdot}$$

$$\xrightarrow[\text{Repeatedly}]{CH_2=CHR} \text{Rad}-[CH_2-\underset{R}{CH}]_n-CH_2-\underset{R}{CH}^{\cdot}$$

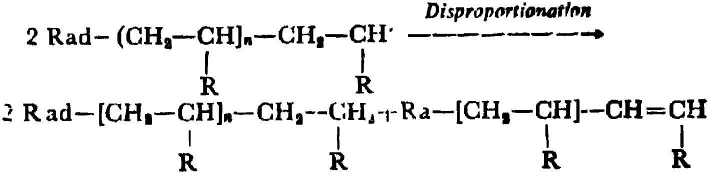
chain-propagating steps

Various chain-termination steps will be union or disproportionation, of two radicals that consume but do not generate radicals.



$$2\ \text{Rad}-[CH_2-\underset{R}{CH}]_n-CH_2-\underset{R}{CH}^{\cdot} \xrightarrow{\textit{Union}}$$

$$\text{Rad}-[CH_2-\underset{R}{CH}]_n-CH_2-\underset{R}{CH}-\underset{R}{CH}-CH_2-[\underset{R}{CH}-CH_2]_n-\text{Rad}$$



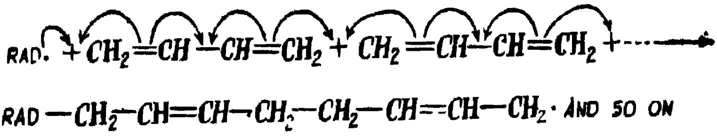
$$2\ \text{Rad}-(CH_2-\underset{R}{CH}]_n-CH_2-\underset{R}{CH}^{\cdot} \xrightarrow{\textit{Disproportionation}}$$

$$2\ \text{Rad}-[CH_2-\underset{R}{CH}]_n-CH_2-\underset{R}{CH_2}+\text{Ra}-[CH_2-\underset{R}{CH}]-\underset{R}{CH}=\underset{R}{CH}$$

Like substituted ethylenes, conjugated dienes also undergo free-radical polymerisation. For example, 1, 3-butadiene gives polybutadiene.

$$\underset{\text{1,3-Butadiene}}{CH_2=CH-CH=CH_2} \longrightarrow \underset{\text{Polybutadiene}}{[-CH_2-CH=CH-CH_2-]_n}$$

The reaction is supposed to proceed as follows :

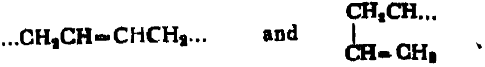


$$\text{RAD}^{\cdot} + CH_2=CH-CH=CH_2 + CH_2=CH-CH=CH_2 + \cdots\longrightarrow$$

$$\text{RAD}-CH_2-CH=CH-CH_2-CH_2-CH=CH-CH_2^{\cdot}\ \text{AND SO ON}$$

Such a polymer differs from polymers of simple alkenes in one very important respect—each unit still contains one double bond.

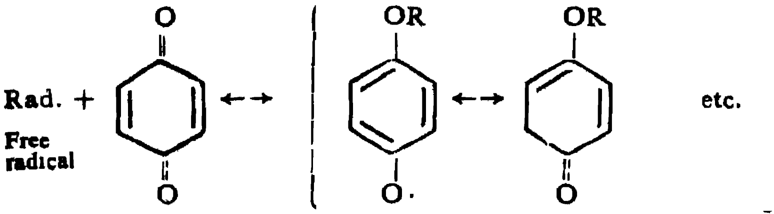
Problem. Free-radical polymerisation of 1,3-butadiene gives macromolecules containing the following two types of units :



$$\ldots CH_2CH=CHCH_2\ldots \quad \text{and} \quad \underset{\underset{CH=CH_2}{|}}{CH_2CH\ldots}$$

Their exact proportion depends on the temperature. How can you account for the two types of units.

Inhibitors. These are substances which retard or inhibit the chain reaction by combining with the free radical to produce an inactive product which cannot continue the chain reaction. Thus each time a free radical is degraded, the growing chain is terminated. Common substances which find use as inhibitors are quinones, iodine and oxygen. Inhibition by benzoquinone can be explained as follows :



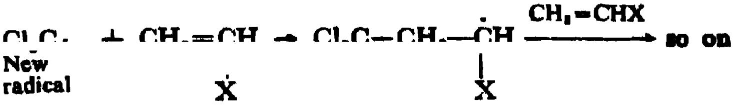
Benzoquinone

Resonance stabilised radical incapable of adding to monomer

Slow oxidation of monomers produces peroxides which act as initiators and thus cause polymerisation of the monomer during storage. To prevent this premature polymerisation of vinyl monomers, these are always mixed with inhibitors before storing.

Chain Transfer Agents. *Properties of a polymer depend upon the length of the chain. This is controlled with the help of certain reagents which can interrupt the growth of a particular chain.* However, the products obtained are capable of starting fresh chains. *Thus the overall rate of polymerisation remains unchanged but the average length of the chain or the average molecular weight of the polymer decreases.* These reagents employed to regulate the molecular weight of the polymer are termed *chain transfer agents* (also termed *telomers*). Some examples of these are toluene, carbon tetrachloride and mercaptans. The action of a chain transfer agent, say CCl_4, can be explained as follows :

$$\underset{\substack{\text{Free radical}\\\text{in the existing}\\\text{chain reaction}}}{\text{Rad.}} + \underset{\substack{\text{chain}\\\text{transfer}\\\text{agent}}}{CCl_4} \longrightarrow \underset{\substack{\textit{(previous chain}\\\textit{terminated)}}}{\text{RadCl}} + \underset{\substack{\text{New}\\\text{radical}\\\text{produced}}}{\cdot CCl_3}$$



$$\underset{\substack{\text{New}\\\text{radical}}}{Cl_3C\cdot} + \underset{\text{Monomer}}{CH_2{=}\underset{X}{CH}} \rightarrow Cl_3C{-}CH_2{-}\underset{X}{\overset{\cdot}{C}H} \xrightarrow{CH_2=CHX} \text{so on}$$

(Fresh chain reaction started)

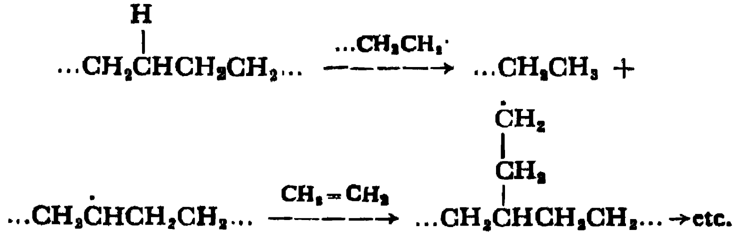
Thus various ways in which the molecular weight of the polymers can be controlled are :

(*i*) *By decreasing the concentration of the initiator.* In the presence of large concentration of the initiator, the number of chains started will be large and controlling their growth will be difficult. As a result, the molecular weight of the polymer will be large.

(*ii*) *By the use of inhibitors*, like quinone.

(*iii*) *By adding chain transfer reagents* like CCl_4 and mercaptans.

Polyethylene obtained by the free-radical process has a highly branched structure due to chain-transfer of a special kind, in which a polymer molecule itself acts as a chain-transfer agent.



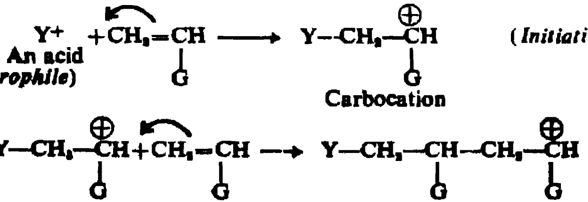
$$\cdots CH_2\overset{H}{\overset{|}{C}}HCH_2CH_2\cdots \xrightarrow{\cdots CH_2CH_2^{\cdot}} \cdots CH_2CH_3 + \cdots CH_2\dot{C}HCH_2CH_2\cdots$$

$$\cdots CH_2\dot{C}HCH_2CH_2\cdots \xrightarrow{CH_2=CH_2} \cdots CH_2\overset{\overset{\dot{C}H_2}{\overset{|}{\overset{CH_2}{|}}}}{C}HCH_2CH_2\cdots \rightarrow \text{etc.}$$

The branch thus planted grows at the point of attack.

8. Ionic Polymerisation.—In addition to the free-radical polymerisation discussed above, polymerisation may involve intermediate ions (cations or anions) in the presence of suitable catalysts as illustrated below :

(*a*) *Cationic polymerisation.* This is believed to take place in the presence of acids, *e.g.*, H_2SO_4, HF or Lewis acids such as $AlCl_3$, $SnCl_4$, BF_3. *Cationic catalysts are usually electrophilic reagents which acquire a share in a pair of pi electrons from the double bond of the monomer.* The polymerisation proceeds via the formation of carbocation as an intermediate as shown below :



$$\underset{\substack{\text{An acid}\\(\textit{An electrophile})}}{Y^+} + CH_2=\underset{G}{\underset{|}{C}H} \longrightarrow \underset{\text{Carbocation}}{Y-CH_2-\overset{\oplus}{\underset{G}{\underset{|}{C}H}}}$$

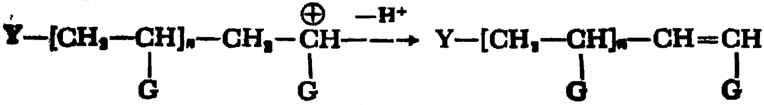
(*Initiation step*)

$$Y-CH_2-\overset{\oplus}{\underset{G}{\underset{|}{C}H}}+CH_2=\underset{G}{\underset{|}{C}H}\longrightarrow Y-CH_2-\underset{G}{\underset{|}{C}H}-CH_2-\overset{\oplus}{\underset{G}{\underset{|}{C}H}}$$

and so on

(*Propagation steps*)

The chain termination step consists in the loss of a proton resulting in the formation of a double bond at the end of the chain. **The resulting molecule becomes deactivated and the chain reaction stops.**



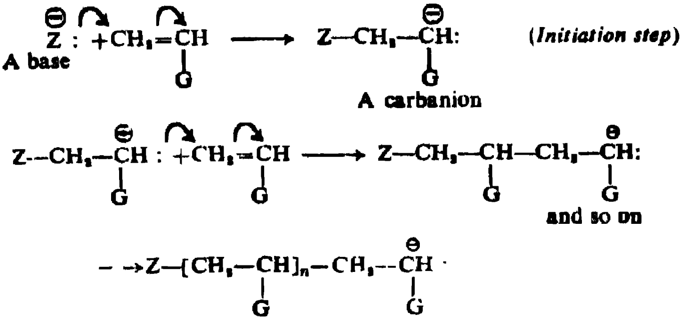
$$Y-[CH_2-\underset{G}{\underset{|}{C}H}]_n-CH_2-\overset{\oplus}{\underset{G}{\underset{|}{C}H}}\xrightarrow{-H^+}Y-[CH_2-\underset{G}{\underset{|}{C}H}]_n-CH=\underset{G}{\underset{|}{C}H}$$

(*Termination step*)

Dimerisation of isobutylene at elevated temperatures in the presence of 60% H_2SO_4 to form 2, 4, 4-trimethyl-2-pentene is an example of various steps involved therein as given on page 1·149.

For successful polymerisation by the cationic process, *electron-releasing groups should be attached to the carbon atom with the double bond in order to stabilise the developing carbocation.* This is the reason why ethene does not polymerise by this process but isobutylene does.

(*b*) ***Anionic polymerisation.*** It proceeds *via* the formation of a carbanion. The chain is initiated by the action of a strong electron donor ($\overset{\ominus}{Z}:$) on a monomer to form a carbanion. The commonly used base is sodamide. The chain then propagates and terminates as usual.



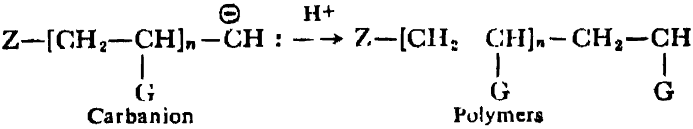
$$\underset{\text{A base}}{\overset{\ominus}{Z}:} + CH_2=\underset{G}{\underset{|}{CH}} \longrightarrow \underset{\text{A carbanion}}{Z-CH_2-\overset{\ominus}{\underset{G}{\underset{|}{C}}}H:} \quad \textit{(Initiation step)}$$

$$Z-CH_2-\overset{\ominus}{\underset{G}{\underset{|}{CH}}}: + CH_2=\underset{G}{\underset{|}{CH}} \longrightarrow Z-CH_2-\underset{G}{\underset{|}{CH}}-CH_2-\overset{\ominus}{\underset{G}{\underset{|}{CH}}}:$$

and so on

$$\longrightarrow Z-[CH_2-\underset{G}{\underset{|}{CH}}]_n-CH_2-\overset{\ominus}{\underset{G}{\underset{|}{CH}}}$$

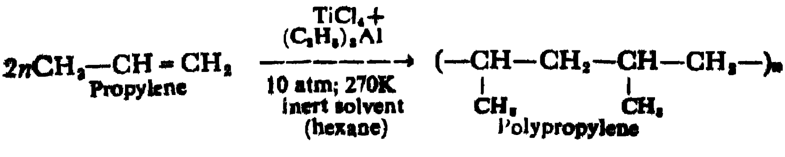
In the termination step the carbanion takes a proton or a cation.



$$\underset{\text{Carbanion}}{Z-[CH_2-\underset{G}{\underset{|}{CH}}]_n-\overset{\ominus}{CH}:} \xrightarrow{H^+} \underset{\text{Polymers}}{Z-[CH_2-\underset{G}{\underset{|}{CH}}]_n-CH_2-\underset{G}{\underset{|}{CH_2}}}$$

Just as cationic polymerisation requires electron-releasing groups in the molecule to stabilise the intermediate carbocation, the anionic polymerisation takes place with monomers which possess electron-attracting groups like CN, COOR, Cl, etc.

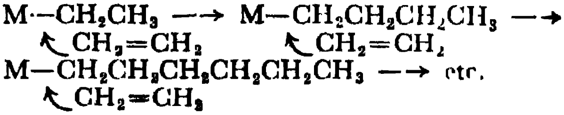
9. **Ziegler-Natta Polymerisation.**—Ethylene and propylene polymerise only at high temperature and pressure. Karl Ziegler and Natta put forward in 1963 that *the polymerisation could be effected in an inert solvent at moderate pressure in the presence of stereospecific catalysts, e.g.*, metal compounds such as $TiCl_4$, $Zr(OR)_4$, etc., together with *co-catalysts* such as R_3Al, $LiAlH_4$, etc. A typical Ziegler catalyst is $TiCl_4$ and $(C_2H_5)_3Al$. The product is usually a mixture of predominantly the stereospecific products. The polymer differs considerably from high pressure polymer. Thus polythene obtained by this method has molecular weight varying from 10,000 to 3,000,000, contains unbranched chain molecules and is more crystalline than high pressure polythene. It has higher density, higher softening point and is tough and flexible. It is inert to acids, alkalis and solvents. Since it is an excellent electrical insulator and can be readily moulded it is used for piping and for coating cables.



$$\underset{\text{Propylene}}{2nCH_3-CH=CH_2} \xrightarrow[\substack{10\text{ atm; }270K\\ \text{inert solvent}\\ \text{(hexane)}}]{TiCl_4+(C_2H_5)_3Al} \underset{\text{Polypropylene}}{(-\underset{CH_3}{\underset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-)_n}$$

Polypropylene obtained by this method is stronger and lighter and has higher softening point than polyethylene. It is used for making wrapping films and ropes.

The mechanism of Zeigler-Natta polymerisation is not clearly understood. It appears to occur with the insertion of alkene molecules into the bond between metal and the growing alkyl group. For example, formation of polyethylene proceeds as under :



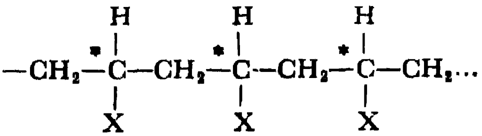
$$\underset{\nwarrow CH_2=CH_2}{M-CH_2CH_3} \longrightarrow \underset{\nwarrow CH_2=CH_2}{M-CH_2CH_2CH_2CH_3} \longrightarrow$$

$$\underset{\nwarrow CH_2=CH_2}{M-CH_2CH_2CH_2CH_2CH_2CH_3} \longrightarrow \text{etc.}$$

Possibly the carbanions are held by the titanium atoms in the catalyst surface by coordination and hence this mode of polymerisation has also been named as **coordination polymerisation**. In recognition of this work Zeigler and Natta were jointly awarded Nobel prize in chemistry in 1963.

10. Stereochemistry of Polymers.—Physical properties of polymers are influenced not only by the nature of the atoms composing their chains but also by the *size, shape and cross-linking of these chains.* Stereochemistry of the polymers is, therefore, very important. Polysaccharides and proteins occurring in nature are optically active and their configuration is fixed by the biochemical process from which they originate. Similarly, natural rubber has been found to be only *cis* compound rather than a mixture of the different possible geometrical isomers. The original configurations of these polymers are largely retained in their commercial applications.

Neoprene, polystyrene, etc. are synthetic vinyl polymers of the general type,



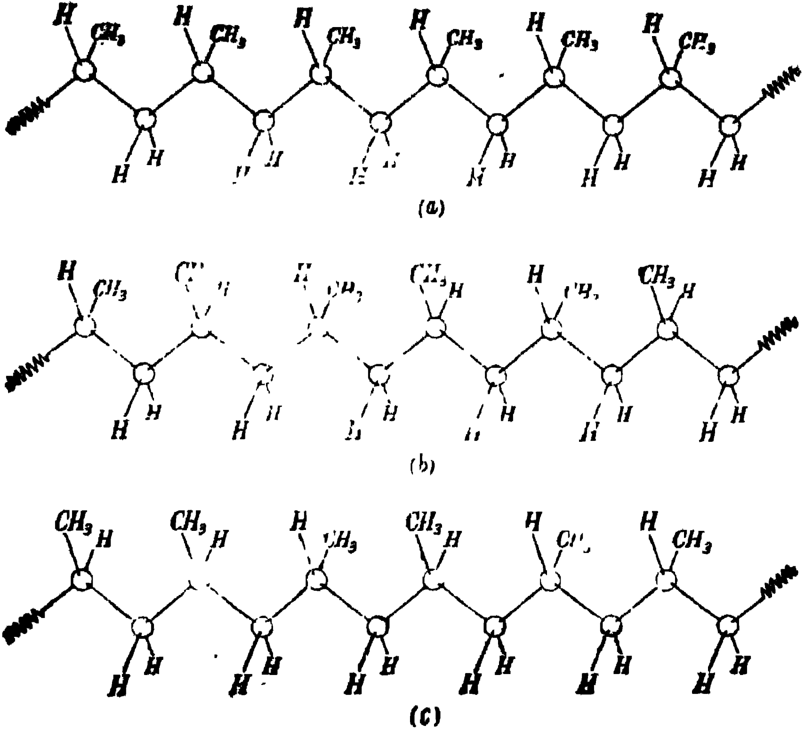
$$-CH_2-\underset{X}{\overset{H}{\overset{*}{C}}}-CH_2-\underset{X}{\overset{H}{\overset{*}{C}}}-CH_2-\underset{X}{\overset{H}{\overset{*}{C}}}-CH_2\cdots$$

in which X=CN, Cl, C_6H_5, CH_3, etc.

In these, every other carbon atom (marked by asterisk) is **asymmetric.** These substances, as usually produced, are probably heterogeneous mixtures of all possible configurations spread irregularly along the chain.

Propylene could polymerise in any of the following three arrangements :

(*i*) **isotactic** with all methyl groups situated in one side of an extended chain ; (*ii*) **syndiotactic**, with methyl groups alternating regularly from side to side and (*iii*) **atactic** having methyl groups distributed at random along the chain (Fig. 56·1).



(*a*) Isotactic polypropylene with all methyl groups on one side of extended chain. It is a highly crystalline, high-melting material which forms strong fibres.

(*b*) Syndiotactic polypropylene with methyl groups alternating regularly from one side to the other side.

(*c*) Atactic polypropylene with methyl groups distributed at random. It is a soft, elastic, rubbery material.

Fig. 56·1—Different polymers of propylene.

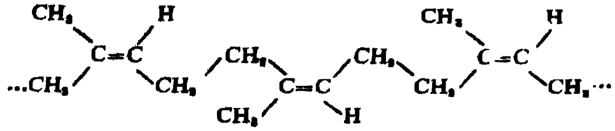
Isotactic propylene is highly crystalline, high melting material that forms strong fibres . The molecules always coil in the same direction and a regular helical spiral arrangement results. Such molecules pack into a neatly crystalline pattern, thus giving the polymer a high m.p. (443 K), and rigidity. The polymer is racemate as there are equal number of right-handed and left-handed chains. The polymer has good insulating (thermal and electrical) properties.

The regular arrangement in syndiotactic polymer also permits more compact arrangement and resembles isotactic polymer.

Atactic polymer has randomly coiled arrangement. Free radical polymerisation gives this variety which is soft, elastic and rubbery material.

Under suitable experimental conditions (catalyst, temperature and solvent) any of these polymers could be manufactured.

With the help of coordination catalysts, it is now possible to polymerise isoprene to a material virtually identical with natural rubber (*cis*-1, 4-polyisoprene).



Natural rubber—*All cis-configuration*

11. **Plasticity.**—The word plastic is misleading, as the commercial products are usually hard, sometimes rigid and sometimes flexible. They are definitely not plastic. Shape of certain substances like sealing wax can be changed under pressure, especially when hot. They are, however, sufficiently viscous to retain shapes of their own, especially when cold. This property is termed plasticity. Commercial plastics have this property at some stage during their manufacture.

12. **Types of Plastics.**—There are two main types of plastics in industry called (*i*) Thermoplastic plastics, and (*ii*) Thermosetting plastics.

(*a*) **Thermoplastic plastics.** *These have long polymer chain with few, if any, chemical bonds acting as* **cross links** *between the chains.* This is shown schematically in Fig. 56·2.

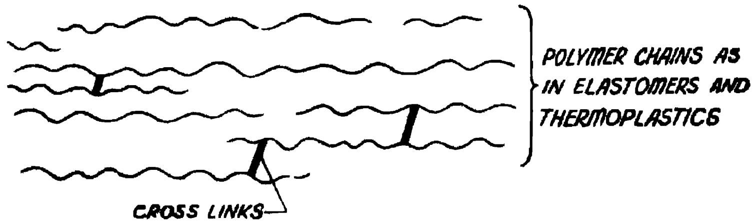


Fig. 56·2—Schematic representation of thermoplastic plastics with a few cross-links.

Such polymers when heated become soft and more or less fluid and then can be moulded into useful shapes.

Cross-links are extremely important in determining the physical properties because they increase the molecular weight and limit the motion of chains with respect to one another.

A thermoplastic plastic when heated repeatedly will soften and flow and when cooled, it hardens. Thus it undergoes reversible changes when heated and cooled. Polystyrene is an example of thermoplastic plastics.

(*b*) **Thermosetting plastics.** *These are normally semi-fluid substances with low molecular weight.* On heating in a mould they become highly cross-linked, thereby forming hard, infusible and insoluble products having a three-dimensional space network of bonds interconnecting the polymer chains (Fig. 56·3).

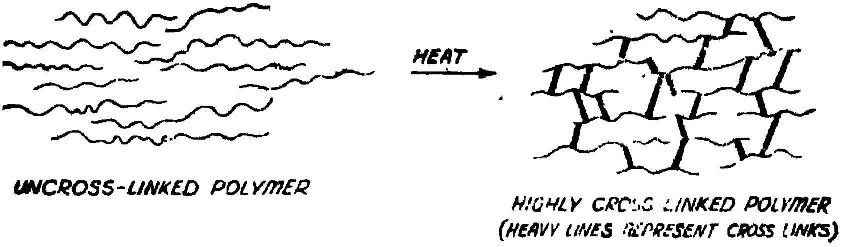

HEAT
UNCROSS-LINKED POLYMER
HIGHLY CROSS LINKED POLYMER
(HEAVY LINES REPRESENT CROSS LINKS)

Fig. 56·3—Schematic representation of the conversion of uncross-linked polymer to a highly cross-linked polymer.

A thermosetting plastic cannot be softened by reheating.

13. **Plasticizers.**—Many times a plastic such as polythene turns out to be too stiff for its intended application. Chemists have found that the addition of certain compounds called plasticizers can render the polymer more flexible. The structure of a polymer largely determines its flexibility. *Polymer chains are intertwined and somewhat aligned in the solid state* and hence the polymer lacks flexibility. *Plasticizers fit between the polymer chains and thus weaken the attractions between the chains, thereby increasing the flexibility.*

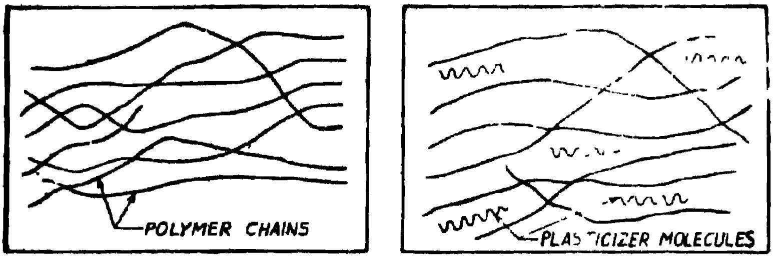


Fig. 56·4—Schematic representation how a plasticizer works.

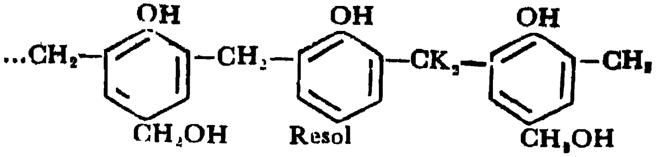
14. **Classification of Resins and Plastics.**—In industry ~~*unfabricated material is called*~~ *the resin while the fabricated product is termed a plastic.* They have been arbitrarily classified on the basis of their composition and source as follows :

Phenol-Formaldehyde Resin (Bakelite). Phenol and formaldehyde undergo condensation polymerisation under two different conditions to give resins.

(*a*) *In presence of dilute acids*, the two react to give *thermoplastics called novolaks* used for the manufacture of cements, varnishes and laminated materials. It is probably a linear polymer. The reaction is known as *Lederer-Manasse reaction (For mechanism see page 2·608)*.

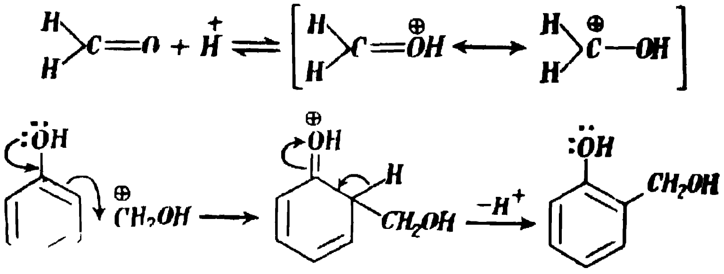
(*b*) In presence of alkalis **resol** is formed which is a *thermoplastic material* used in the manufacture of adhesives. This too has,

long chain macromolecules but with many unused CH_2OH groups.



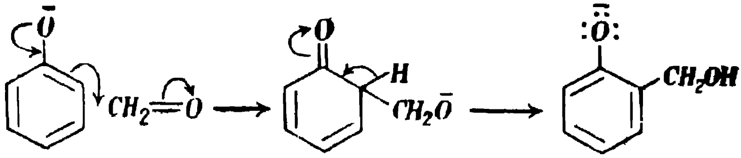
Resol

Acid-catalysed

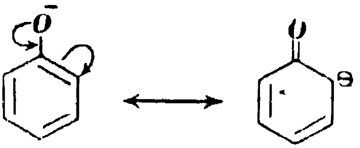


Lederer-Manasse reaction

Base-catalysed

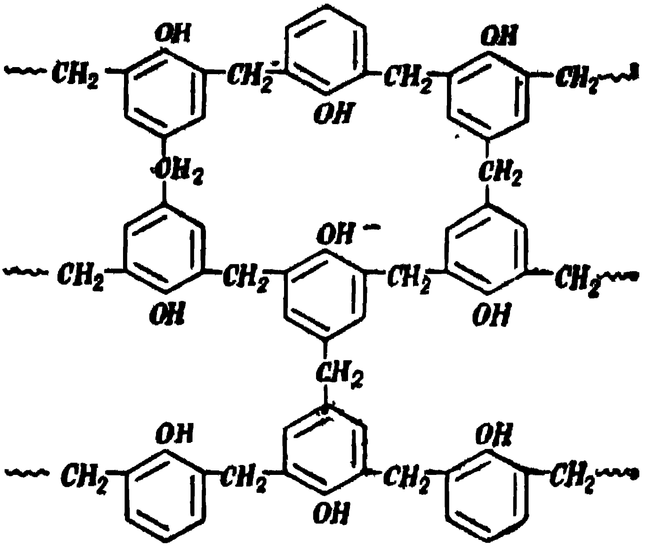


Phenoxide is a species which can lay claim to be a carbanion only because of the π delocalisation that results in the transfer of negative charge from oxygen to carbon in the phenoxide ion.



On heating cross linkages are formed with formation of a three-dimensional thermosetting resin, bakelite Phenol is a polyfunctional reactant having one para and two ortho positions open to attack. During moulding further condensation occurs in which new methylene groups derived from the uncondensed CH_2OH groups form cross links between molecular chains resulting in a three dimensional lattice

Trifunctional monomers yield thermoplastic resins and polyfunctional monomers produce thermosetting resins.



Bakelite—a three dimensional thermosetting resin

Procedure. Novolak is prepared, mixed with fillers like wood flour and 12-14% hexamethylenetetramine and heated. The latter when heated is a source of HCHO and catalyst NH_3. The aldehyde gives rise to new methylene bridges resulting in cross-linking to give a three-dimensional polymer.

(2) **Urea-Formaldehyde Resins.** Urea and formaldehyde react to give resins which are widely used in the manufacture of crease-resisting textiles, adhesives, plywood, moulding powder, ating paper and fibres.

These are prepared by dissolving urea in aqueous formaldehyde below 280K and affecting condensation at about 400K. Water is removed under reduced pressure. The primary condensation products are monomethylol urea which can be abtained at room temperature and dimethylol-urea which can be obtained at 330K in neutral or slightly alkaline solution.

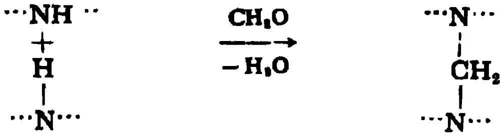
$$NH_2CONH_2 + CH_2{=}O \xrightarrow{\text{Room temp.}} \underset{\text{Monomethylolurea}}{H_2NCONHCH_2OH}$$

$$NH_2CONH_2 + 2CH_2{=}O \xrightarrow[\text{neutral or slightly alkaline}]{330K} \underset{\text{Dimethylolurea}}{HOCH_2NHCONHCH_2OH}$$

$$\xrightarrow{+\,2\,NH_2CONH_2} NH_2CONH-CH_2NHCONHCH_2-NHCONH_2$$

$$\xrightarrow[+\,HCHO]{NH_2CONH_2} \underset{\text{Polymer chain}}{NH_2CO(NHCH_2NHCO)_n\,NHCH_2OH}$$

The — NH— groups appearing in the linear polymer become the sites of new interactions with HCHO which cross-link the linear chain into a network of high molecular weight. This can be represented schematically as follows :



$$\begin{array}{c}\cdots NH\cdots\\ +\\ H\\ |\\ \cdots N\cdots\end{array} \xrightarrow[-H_2O]{CH_2O} \begin{array}{c}\cdots N\cdots\\ |\\ CH_2\\ |\\ \cdots N\cdots\end{array}$$

Depending on the conditions employed the polymerised products may be water soluble resins, water insoluble but thermoplastic or thermosetting plastics.

It is a colourless resin which is mixed wish fillers like wood flour, or cellulose pulp and desired dye before moulding. These are valued on account of their hardness, resistance to wear and stable colour.

(3) **Polymer resins**, for example, vinyl resins, acryloid resins, teflon and polystyrene. Some of these are discussed below :

(*i*) **Teflon**. Teflon is a polymer of tetraflouroethylene ($CF_2=CF_2$). The monomer is prepared by the action of hydrofluoric acid and antimony trifluoride on chloroform..

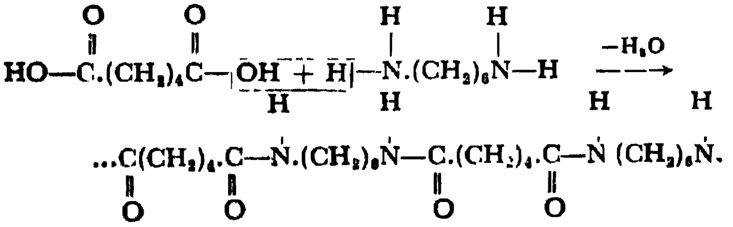
$$CHCl_3 \xrightarrow[HF]{SbF_3} CHF_2Cl \xrightarrow{1070K} CF_2=CF_2 + 2HCl$$

This on polymerization gives teflon.

$$\underset{\text{Tetrafluoroethylene}}{n\,CF_2=CF_2} \xrightarrow{870\text{-}1020K} \underset{\text{Teflon}}{(-CF_2-CF_2-)_n}$$

It is a thermoplastic polymer with a high softening point (600K). It is very tough and difficult to work. It is inert to most chemicals except fluorine and molten alkali metals. It is non-inflammable and not attacked by concentrated acids and alkalis. It withstands high temperatures. Its electrical properties make it an ideal insulating material for high frequency installation.

(*ii*) **Nylon-66.** Nylon-66 is a condensation copolymer formed by the reaction between adipic acid [$HOOC(CH_2)_4.COOH$] and hexamethylenediamine [$H_2N.(CH_2)_6NH_2$]. Both the monomer units consist of 6 carbon atoms and is, therefore, named nylon-66.

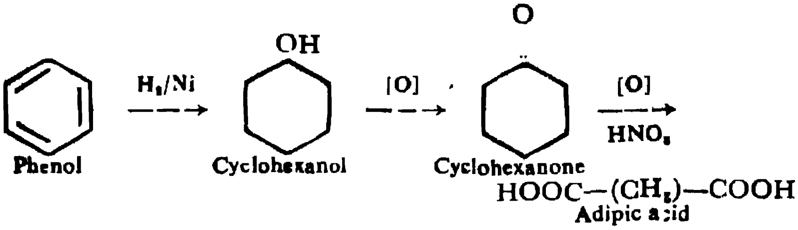


$$HO-\overset{\overset{O}{\|}}{C}.(CH_2)_4\overset{\overset{O}{\|}}{C}-\underset{H}{\boxed{OH + H}}-\underset{H}{\overset{\overset{H}{|}}{N}}.(CH_2)_6\overset{\overset{H}{|}}{N}-H \xrightarrow{-H_2O}$$

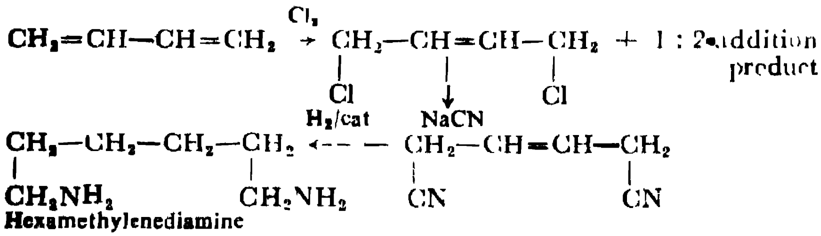
$$\ldots\underset{\underset{O}{\|}}{C}(CH_2)_4.\underset{\underset{O}{\|}}{C}-\overset{H}{N}.(CH_2)_6\overset{H}{N}-\underset{\underset{O}{\|}}{C}.(CH_2)_4.\underset{\underset{O}{\|}}{C}-\overset{H}{N}(CH_2)_6\overset{H}{N}.$$

Nylon-66 (*a condensation copolymer*)

Adipic acid is obtained from phenol while hexamethylenediamine is obtained from butadiene,



Preparation of hexamethylenediamine



$$CH_2{=}CH{-}CH{=}CH_2 \xrightarrow{Cl_2} \underset{Cl}{CH_2}{-}CH{=}CH{-}\underset{Cl}{CH_2} + 1:2\text{-addition product}$$

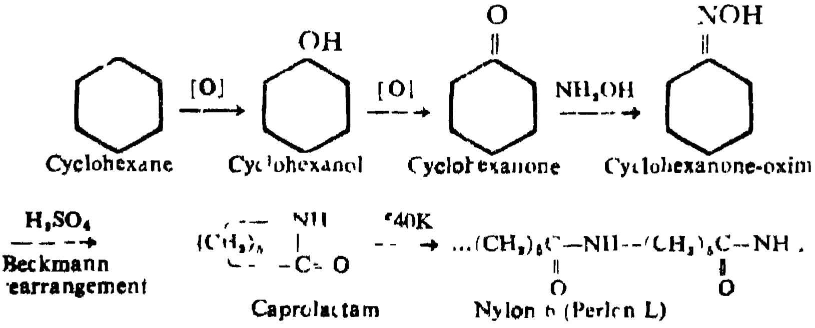
$$\xrightarrow{NaCN} \underset{CN}{CH_2}{-}CH{=}CH{-}\underset{CN}{CH_2} \xrightarrow{H_2/cat} \underset{CH_2NH_2}{CH_2}{-}CH_2{-}CH_2{-}\underset{CH_2NH_2}{CH_2}$$

Hexamethylenediamine

It is a thermoplastic polymer. When extruded above its melting point (536K) through spinneret, it give nylon fibre which is extremely tough and resistant to friction. It possesses greater tensile strength, elasticity and lustre than any natural fibre. It is chemically inert and is fabricated into sheets, bristles and textile fibres.

(*iii*) **Perlon L or Nylon-6.** A polyamide closely related to nylon known as perlon L (Germany) or as Nylon-6 (USA) is prepared by prolonged heating of caprolactum at 530-540K.

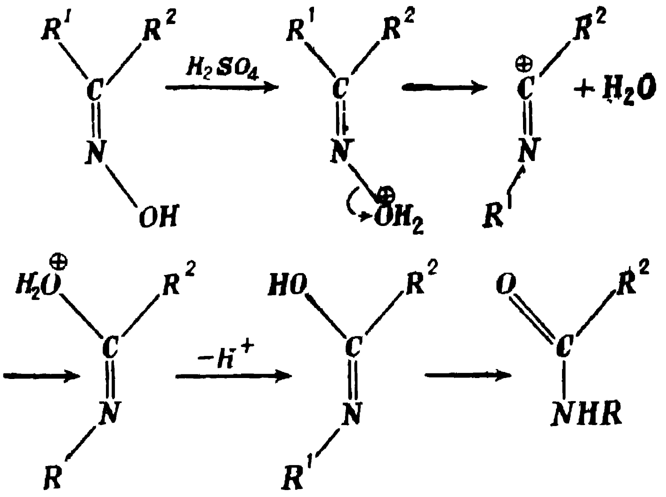
Caprolactum is obtained by *Beckmann rearrangement* of cyclohexanone oxime,



Beckmann rearrangement. Ketoximes on treatment with reagents like PCl_5, H_2SO_4, H_3PO_4, etc. undergo Beckmann rearrangement to form an acid amide.

$$\underset{\text{Ketoxime}}{Ar_2C{=}NOH} \longrightarrow \underset{\text{Acid amide}}{ArCONHAr}$$

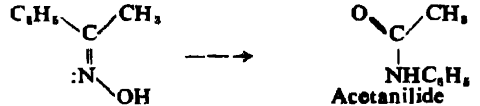
The rearrangement is intramolecular involving 1,2-shift as follows :



(When PCl_5 is used, replace $\overset{\oplus}{O}H_2$ by $OPCl_4$)

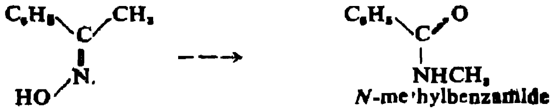
It has been demonstrated *that it is always the anti-R group that migrates in the Beckmann rearrangement.*

This rule will be illustrated by the following products of the reaction



Acetanilide

C_6H_5 being anti-R has migrated)

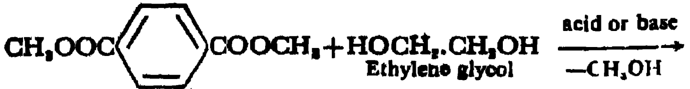


N-methylbenzamide

(CH_3 being anti-R has migrated)

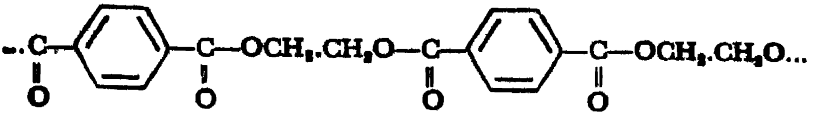
The fibre is practically identical to Nylon in properties.

(*iv*) **Dacron.** A polyester of terephthalic acid and ethylene glycol is used in the production of the synthetic fibre. This fibre has wrinkle resistance and dimensional stability. It is resistant to moth, mildew and abrasion. The polymer is made by an ester exchange reaction between methyl terephthalate and ethylene glycol.



Ethylene glycol

Methyl terephthalate

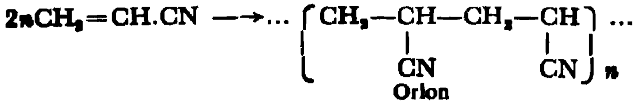


Dacron (*A Polyester*)

This is an example of condensation polymerisation since monomer molecules are combined with the loss of simple molecule, methanol.

(*v*) **Saran.** It is a copolymer of vinylidene chloride (85%) and vinyl chloride (15%). It has a very high molecular weight of 20,000 which is comparable to that of vinyon. Its softening point is considerably high (390—410K). Fibres for dress material can be obtained by melt-spinning, immersion in hot water (to prevent crystallisation) and mechanical stretching.

(*vi*) **Orlon fibre** (USA). It is made from polyacrylonitrile. It is insoluble in common solvents but dissolves in *N*, *N*-dimethylformamide, *N*, *N*-dimethylacetamide, Nitrophenols, etc. The fibre has unusual dimension stability in the dry and wet states. It has excellent resistance to sunlight, outdoor exposure, micro-organisms, acids and solvents. It can be made to look like silk or wool. The textiles feel warm to hand.



$$2nCH_2=CH.CN \longrightarrow \ldots\left[CH_2-\underset{CN}{\underset{|}{C}H}-CH_2-\underset{CN}{\underset{|}{C}H}\right]_n\ldots$$

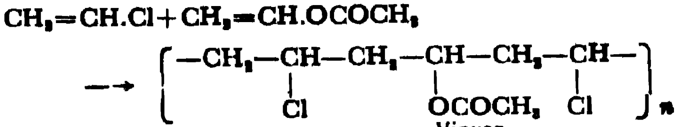
Orlon

(*vii*) **Dynel or Vinyon N.** It is a copolymer of acrylonitrile and vinyl chloride containing about equimolar quantities of the two monomers and can be spun into a fibre from acetone solution.

(*viii*) **Acrilon.** It is polyacrylonitrile modified with vinyl acetate.

(*ix*) **Vinyl fibres.** Polymer derived from vinyl chloride and vinyl acetate were developed as plastics and resins but later the technique of emulsion copolymerisation was found applicable to the production of a variety of vinyl copolymers useful as fibres.

Vinyon is a copolymer of vinyl chloride (88%) and vinyl acetate (12%).



$$CH_2=CH.Cl+CH_2=CH.OCOCH_3$$

$$\longrightarrow \left[-CH_2-\underset{Cl}{\underset{|}{C}H}-CH_2-\underset{OCOCH_3}{\underset{|}{C}H}-CH_2-\underset{Cl}{\underset{|}{C}H}-\right]_n$$

Vinyon

Vinyon is highly resistant to chemicals but its low softening point (338K) limits its use as a textile fibre.

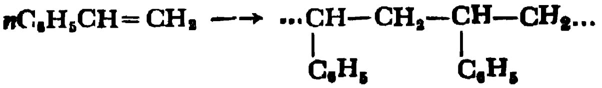
(*x*) **Polyethylene** $(\ldots CH_2-CH_2\ldots)_n$. Polymerisation of liquid ethylene at high temperature and pressure gives a resin of low softening point (383K). It can be melt-spun or moulded. The material is tough, flexible and highly insulating and water resisting. It is unique in having low specific gravity (0·22). It is used for electric insulation.

$$nCH_2{=}CH_2 \longrightarrow \underset{\text{Polythene}}{(\ldots CH_2{-}CH_2\ldots)_n}$$

(*xi*) **Polypropylene.** The linear polymer obtained by treatment of propylene with the Zeigler catalyst is a crystalline material that shows much promise in the manufacture of wool like fibre.

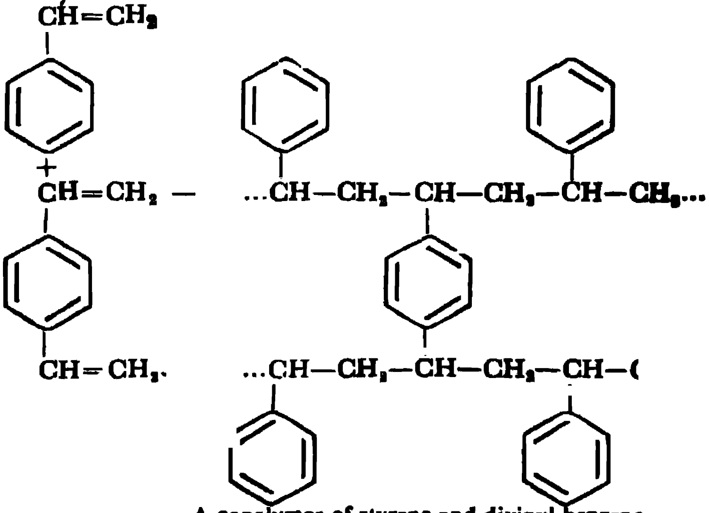
(*xii*) **Polystyrene.** It is obtained by linear polymerisation of styrene in the presence of peroxides (*e.g.*, dibenzoyl peroxide) or sodium or on exposure to sunlight Styrene is obtained by dehydrogenating ethylbenzene. It contains a conjugated system of double bonds.

$$C_6H_5CH_2CH_3 \xrightarrow[870K]{ZnO} \underset{\text{Styrene}}{C_6H_5CH{=}CH_2} + H_2$$



$$nC_6H_5CH{=}CH_2 \longrightarrow \ldots\underset{C_6H_5}{CH}{-}CH_2{-}\underset{C_6H_5}{CH}{-}CH_2\ldots$$

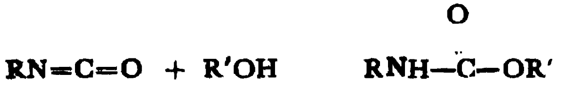
Cross-linking is introduced to a controlled extent by using traces of divinylbenzene.



A copolymer of styrene and divinyl-benzene

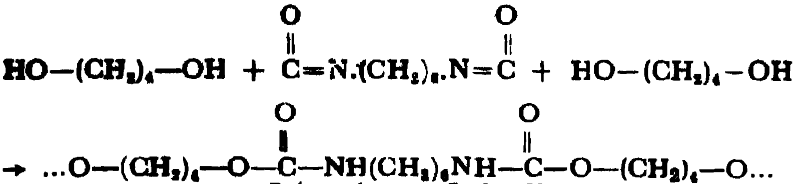
It is a light transparent thermoplastic material with excellent insulating properties and good mechanical strength. It is used in injection moulding. It has a high tensile strength and does not absorb moisture. Its high dielectric constant makes it very useful in radio-insulation. It is also used in the manufacture of storage battery cases, gramophone records, emulsion paints, light weight packing materials and a wide variety of household goods such as egg boxes and lining material for refrigerators.

(*xiii*) **Polyurethans.** The product of reaction between an isocyanate and an alcohol is called urethan,



$$RN{=}C{=}O + R'OH \qquad RNH{-}\overset{O}{\overset{\|}{C}}{-}OR'$$

Diisocyanates like hexamethylene diisocyante and tetramethylene glycol are both bifunctional and undergo step-reaction polymerisation to produce polyurethans.



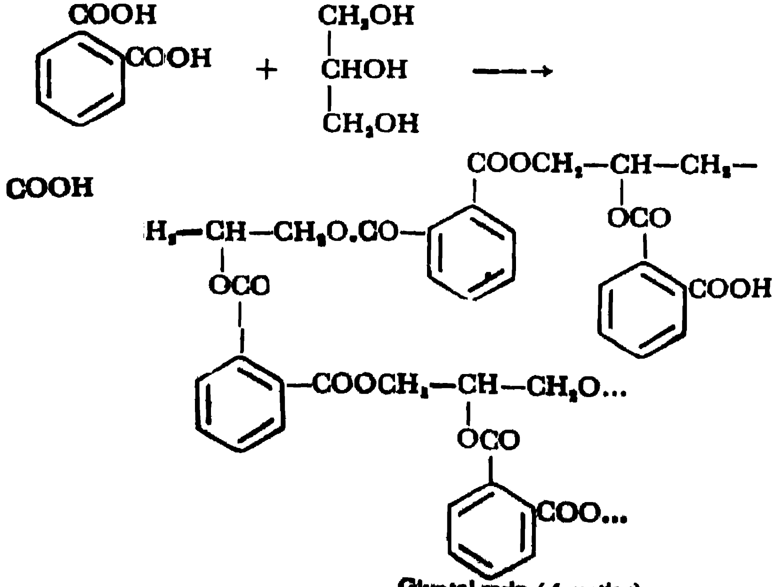
$$HO{-}(CH_2)_4{-}OH + \overset{\overset{O}{\|}}{C}{=}N.(CH_2)_6.N{=}\overset{\overset{O}{\|}}{C} + HO{-}(CH_2)_4{-}OH$$

$$\rightarrow \ldots O{-}(CH_2)_4{-}O{-}\overset{\overset{O}{\|}}{C}{-}NH(CH_2)_6NH{-}\overset{\overset{O}{\|}}{C}{-}O{-}(CH_2)_4{-}O\ldots$$

Polyurethan (Perlon U)

It is a thermoplastic fibre and is used in the manufacture of combs, etc. The linear product can react with more of the monomeric diisocyanate to give cross-linkages resulting in the formation of synthetic rubber which is used in the manufacture of tyres and shoe soles.

(*xiv*) **Glyptals or Alkyds.** It is a polyester having cross-linkages and is manufactured by the action of phthalic acid or its anhydride or other dicarboxylic acids on glycerol. It is a thermosetting plastic and finds use chiefly as coating in the lacquer and paint industry.



Glyptal resin (*A section*)

RUBBER AND RUBBER SUBSTITUTES

15. Natural Rubber.—Elastomers are substances which can be stretched readily and when released can retract rapidly to their original form. Rubber is a common example of an elastomer.

Natural rubber obtained from latex which is coagulated with acetic or formic acid and then subjected to treatment like squeezing, rolling, milling, vulcanizing, etc.

Properties. Crude rubber is tough, elastic, solid (sp. gr. 0·915). It is soft and sticky becoming more so with rise of temperature. It has low tensile strength and has elasticity over a narrow range of temperature. Vulcanisation increases tensile strength and helps to retain elasticity over a wide range of temperature. Pure rubber is transparent, amorphous solid which on stretching or prolonged cooling becomes crystalline. It is insoluble in water, alcohol, acetone, dilute acids and alkalis but soluble in ether. It freely dissolves in CS_2, CCl_4, petrol and turpentine.

Structure :

(*i*) *Molecular formula.* Destructive distillation of rubber gives mainly isoprene and dipentene suggesting the presence of a repeating isoprene unit, *i e.*, it is a polyisoprene with formula $(C_5H_8)_n$. Isoprene on polymerisation gives a rubber-like substance. Its molecular weight is of the order 300,000.

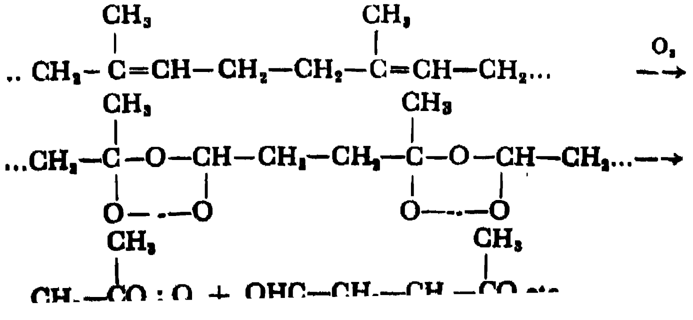
Faraday assigned it the empirical formula C_5H_8 as early as 1825.

(*ii*) *Presence of one double bond per isoprene unit,* is shown by the following ·

(*a*) Addition of halogens and halogen acids to give $(C_5H_8Br_2)_n$ and $(C_5H_9Cl)_n$.

(*b*) Formation of ozonide $(C_5H_8O_3)_n$

(*iii*) *Head to Tail Linking.* Harries found that products of ozonolysis of rubber were laevulaldehyde and its peroxide + laevulinic acid + small quantities of CO_2, HCOOH and succinic acid.



$$\cdots CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_2-CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_2\cdots \xrightarrow{O_3}$$

$$\cdots CH_2-\underset{\underset{O-}{|}}{\overset{\overset{CH_3}{|}}{C}}-O-\underset{\underset{-O}{|}}{CH}-CH_2-CH_2-\underset{\underset{O-}{|}}{\overset{\overset{CH_3}{|}}{C}}-O-\underset{\underset{-O}{|}}{CH}-CH_2\cdots \longrightarrow$$

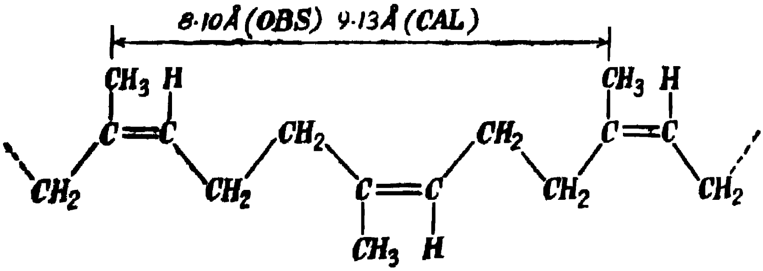
$$\overset{\overset{CH_3}{|}}{CH_2-CO}:O + OHC-CH_2-CH_2-\overset{\overset{CH_3}{|}}{CO}\cdots$$

$$CH_3COCH_2CH_2CHO \dashrightarrow CO_2 + HOOC.CH_2CH_2COOH$$

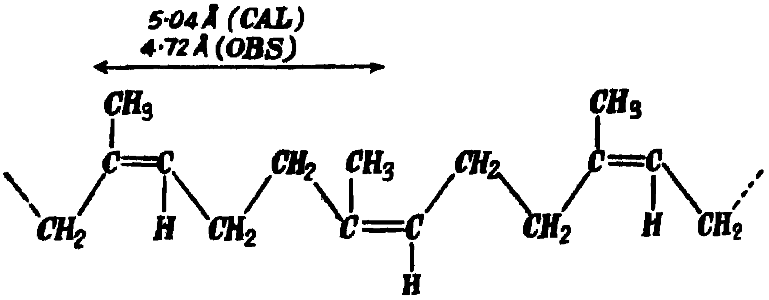
$$\Big|^{O}\!\!\rightarrow CH_3COCH_2CH_2COOH$$

Laevulinic acid

(*iv*) X-ray diffraction study reveals it being composed of long chains of isoprene units arranged in cis form of the double bonds (Bunn, 1942), Gutta-percha, however, has these units arranged in trans form. It is hard and has very low elasticity.



Rubber (*cis* form)



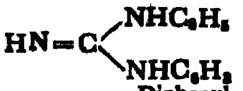
Gutta percha (*trans* form)

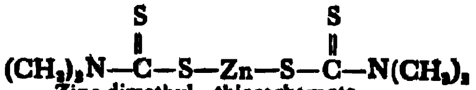
Lengths of the chain repeat units in the two are 8·10Å and 4·72Å.

Proposed structure is in agreement with IR spectra and linear shape of the molecule is confirmed by the viscosity measurement of rubber solution.

16. **Vulcanisation of Rubber.**—It is the process discovered by Charles Goodyear in 1893 to modify the properties of natural rubber, *viz.*, elasticity, tensile strength, resistance to abrasion (friction) and being practically insoluble in usual solvents.

(*a*) *Hot vulcanisation.* Raw dry rubber is heated with sulphur (5-8% depending upon requirement), ZnO (5%) — a filler, and an accelerator (0·5 to 1%) at 400-440K for about half an hour. More the quantity of sulphur, tougher the rubber becomes after vulcanisation, *e.g.*, 50% sulphur gives ebonite. In general an vulcanization takes place at room temperature. Some examples of accelerators are :


Diphenyl guanidine

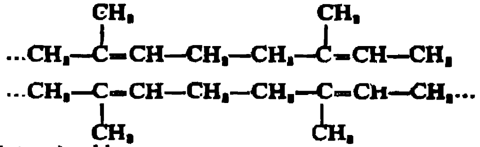

Zinc dimethyl thiocarbamate

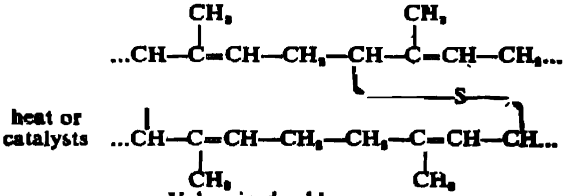
$$(CH_3)_2N-\overset{\overset{S}{\|}}{C}-S-Zn-S-\overset{\overset{S}{\|}}{C}-N(CH_3)_2$$

ZnO also acts as an accelerator.

Heat is not essential, *e.g.*, dipping the article in S_2Cl_2 dissolved in CS_2 etc. in cold vulcanizes rubber.

Mechanism of Vulcanisation. It is believed that double bonds in natural rubber permit formation of sulphur bridges between different chains. These cross links remove the tackness of untreated rubber.


Natural rubber



Vulcanized rubber

The presence of thioether linkages can he detected by their reaction with methyl iodide to form sulphonium iodide

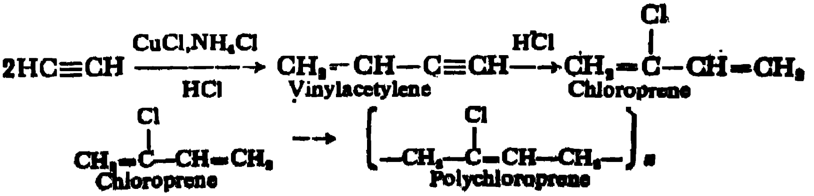
$$>S + CH_3I \longrightarrow >S^+Me + I^-$$

The function of accelerators is to increase the rate of reaction and make vulcanisation take place at relatively lower temperature.

SYNTHETIC RUBBERS

17. **Polychloroprene** (*Neoprene, Dieprene*). Polychloroprene was the first commercially successful rubber substitute manufactured in the United States.

It is obtained by free radical polymerisation of chloroprene obtained from acetylene.



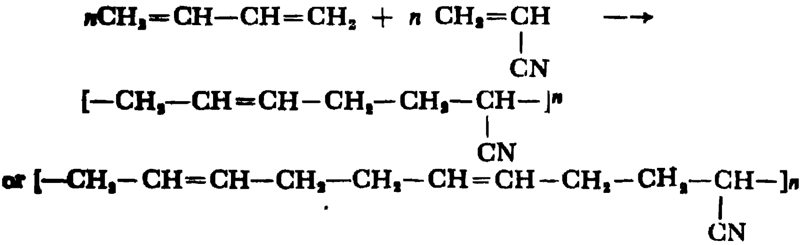
$$2HC\equiv CH \xrightarrow[HCl]{CuCl,NH_4Cl} CH_2=CH-C\equiv CH \xrightarrow{HCl} CH_2=\overset{\overset{Cl}{|}}{C}-CH=CH_2$$

$$CH_2=\overset{\overset{Cl}{|}}{C}-CH=CH_2 \longrightarrow \left[-CH_2-\overset{\overset{Cl}{|}}{C}=CH-CH_2-\right]_n$$

It is a thermoplastic and need not be vulcanised by heating with sulphur but is compounded with other suitable ingredients such as magnesia, wood resin and zinc oxide prior to its use. It is a good general purpose rubber and superior to natural rubber as it is resistant to the action of air, heat, light, abrasion, chemicals, petrol, ozone, alkalis and acids below 50% strength. It is used for making transmission belts, printing rolls and flexible tubing employed for conveyance of oil and petrol.

18. **Buna Rubbers.**—Butadiene polymerises in the presence of sodium to give a rubber substitute, *viz.*, Buna, and was first produced in Germany. It it is of two types ·

(*a*) **Buna-N or GRA.** (*General purpose Rubber Acrylonitrile*). It is the synthetic rubber obtained by copolymerisation of one part of acrylonitrile and two parts of butadiene.



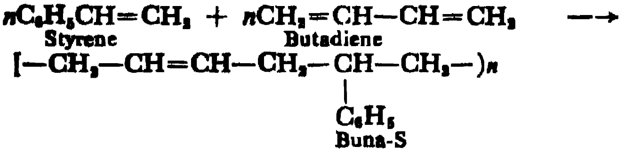
$$n\mathrm{CH_2{=}CH{-}CH{=}CH_2} + n\,\mathrm{CH_2{=}\underset{\substack{|\\ CN}}{CH}} \longrightarrow$$

$$[\mathrm{-CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}\underset{\substack{|\\ CN}}{CH}{-}}]_n$$

$$\text{or } [\mathrm{-CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}\underset{\substack{|\\ CN}}{CH}{-}}]_n$$

It is also known as Per bunan. It is more rigid, responds less to heat treatment and is very resistant to swelling action of petrol, lubricating oils and many other organic solvents. Hence it finds use in fuel tanks.

(*b*) **Buna-S or GRS.** (*General purpose Rubber Styrene*). It is a co-polymer of three moles of butadiene and one mole of styrene and is an elastomer. It is obtained as a result of free radical co-polymerisation of its monomers.



$$\underset{\text{Styrene}}{n\mathrm{C_6H_5CH{=}CH_2}} + \underset{\text{Butadiene}}{n\mathrm{CH_2{=}CH{-}CH{=}CH_2}} \longrightarrow$$

$$\underset{\text{Buna-S}}{[\mathrm{-CH_2{-}CH{=}CH{-}CH_2{-}\underset{\substack{|\\ C_6H_5}}{CH}{-}CH_2{-}})_n}$$

It is generally compounded with carbon black and vulcanised with sulphur. It is extremely resistant to wear and tear and, therefore, finds use in the manufacture of tyres and other mechanical rubber goods.

QUESTIONS

Essay Type :

1 Write short notes on :

(*a*) Polymerisation and its types. (*b*) Polymers and their types.

(*c*) Free-radical mechanism for polymerisation of alkenes and dienes.

(*d*) Rubber and rubber substitutes. (*e*) Vulcanization of rubber.

2. What do you understand by ionic polymerisation and stereoselective synthesis ?

3. Give the structure of the monomer from which each of the following polymers would most likely be made :

(*a*) Orlon (fibres, fabrics),

$\ldots CH_2CH(CN)CH_2CH(CN)\ldots$;

(*b*) Saran (packaging film, seat covers),

$\ldots CH_2CCl_2CH_2CCl_2\ldots$;

(*c*) Teflon (chemically resistant articles),

$\ldots CF_2CF_2CF_2CF_2\ldots$;

4. What are plastics ? What do you understand by a monomer and a polymer ? Give examples.

5. What are the two main types of plastics ? In what respects do they differ from each other ?

6. Write short notes on any three of the following :

(*i*) Teflon ; (*ii*) Bakelite ; (*iii*) Nylon ; (*iv*) Orlon ; (*v*) Dacron.

Short Answer Type :

1. Name the monomers in the following polymers :

(*i*) Polythene ; (*ii*) PVC ; (*iii*) Teflon ; (*iv*) Nylon ; (*v*) Orlon.

2. What is plasticity ?

3. What is the effect of heating on (*i*) thermoplastic plastics, and (*ii*) thermosetting plastics ?

4. What is a plasticizer ?

5. What is copolymer ? What is a condensation polymer ?
(*Delhi B.Sc. Hons. 1982*)

6. Name the monomer in—

(*i*) Natural rubber, (*ii*) Polychloroprene, (*iii*) Buna-S and Buna-N.

7. What do you understand by cross-linking in synthetic plastics ? Explain with suitable example. What is the effect of heat on such plastics ?
(*Delhi B.Sc. Hons. 1976*)

8. Give the stepwise preparation of Teflon. Mention its uses.
(*Delhi B.Sc. Hons. 1976*)

9. Discuss the mechanism of vinyl Polymerisation.
(*Delhi B.Sc. Hons. 1976*)

10. Write a short note on Polymerisation. (*Delhi B.Sc. Hons. Sub. 1977*)

11. Write a short note on 'Addition Polymerisation'.
(*Delhi B Sc. Hons. 1977*)

12. Write a brief note on 'Condensation Polymerisation'.
(*Delhi B.Sc. Hons. 1977*)

13. How will you synthesise the following :

(*i*) Terylene, (*ii*) Buna-N ?

Give equations for the reactions involved. (*Delhi B.Sc. Hons. 1977*)

14 What are the thermoplastic and thermosetting polymers ? Explain the difference between them by taking suitable examples of each.
(*Delhi B.Sc. Hons. 1982*)

15. Explain the polar and free-radical mechanism of polymerisation of alkenes. (*Madras B.Sc. 1980*)

16. Discuss the mechanism of addition in synthesis of orlon.
(*Delhi B.Sc. Hons. 1978*)

17. (*a*) What are ester-exchange polymerisation reactions ?

(*b*) Describe the application of copolymerisation in rubber industry
(*Delhi B.Sc. Hons. 1978*)

18. (*a*) Define syndiotactic polymers.

(*b*) What are plasticizers ? (*Delhi B.Sc. Hons. 1979*

19. Give the mode of formation and uses of the following :

(*a*) Neoprene (*b*) Nylon (*c*) Rayon (*d*) Teflon. (*Delhi B.Sc. Hons. 1979*)

20. (*a*) Discuss the mechanisms of cationic and free radical polymerisations.

(*b*) Explain the difference between addition and condensation polymers giving examples for each.

(*c*) How is polyurethane foam prepared ? (*Delhi B.Sc. Hons. 1981*)

21. How is nylon-66 obtained ? (*Delhi B.Sc. Hons. 1981*)

22. What type of alkene derivatives are polymerised with the help of anions and cations as catalysts ? (*Delhi B.Sc., Hons. 1982*)

23. Give in detail the preparation of a synthetic fibre *either* from petroleum fractions *or* from coal-tar fractions, as raw materials.
(*Delhi B.Sc. Hons. 1982*)

24. (*a*) What is addition polymerisation and condensation polymerisation?

(*b*) Give free radical mechanism for addition polymerisation.
(*Delhi B Sc. 1982*)

13

Colour and Dyes

1. Colour Sensation.—Colour has always played an important role in the life of man. Dyes and pigments have been an important article of commerce since time immemorial. Let us understand how do we get a sensation of colour.

White light is made of seven different colours. These are violet, indigo, blue, green, yellow, orange and red having wavelengths between 400 nm and 750 nm. When white light falls on a substance, it may be—

(*i*) Totally reflected,
(*ii*) Partially reflected, or
(*iii*) Totally absorbed.

When the white light is totally reflected, the substance appears white and when it is totally absorbed, the substance appears to be black. When a part of the incident light is absorbed and the rest reflected, the colour of the substance is the colour of the reflected light. If only a single band is absorbed, the colour of the substance is the complementary colour of the absorbed light band. Relationship between the wavelengths of the light band absorbed and the visible colour of the substance is given in the table below :

Wavelengths absorbed (*nm*)	Colour absorbed	Visible colour (*Complementary*)
400—435	violet	yellow-green
435—480	blue	yellow
480—490	green-blue	orange
490—500	blue-green	red
500—560	green	purple
560—580	yellow-green	violet
580—595	yellow	blue
595—605	orange	green-blue
605—750	red	blue-green

If only one of the band is reflected and all the rest are absorbed, the colour of the substance is that of the reflected band. For example, if a substance absorbs all the bands except blue, it will appear blue. Thus the substance may appear blue—

(*i*) either because it absorbs only the yellow band (wavelength 580-595 nm) of the incident white light and reflects all the rest,

(*ii*) or because it absorbs all the bands except blue (wavelength 435-480 nm) which it reflects.

In practice, substances do not reflect only one band of wavelengths but reflect a mixture of them. For example, malachite green reflects in addition to green light, small amounts of red, blue and violet.

2. **Dyes and Dyeing.**—Coloured substances used for colouring various fabrics are called *dyes.* All coloured substances, however, are not dyes. Requisites of a true dye are :

(*i*) It must have a suitable colour.

(*ii*) It must be able to attach itself to the material from solution or to be capable of being fixed on it.

(*iii*) When fixed it must be fast to light and washing. For this it must be resistant to the action of water, acids and alkalis, particularly the latter due to the alkaline nature of washing soda and washing soap.

Previously, dyes were obtained from animal and vegetable sources. Today most of the available dyes are synthetic dyes prepared from aromatic compounds.

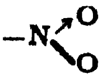
The mechanism of dyeing differs with the nature of the material whether it is protein, cellulose or synthetic fibre. Dyeing of wool and silk was once considered to be a chemical process. Herein the acidic or basic groups in a dye combined with basic or acidic groups in the protein. At present it is believed that acidic or basic groups in the dye help in the initial adsorption of the dye on the surface of the fibre. This is followed by solution and diffusion of the dye into the fibre.

3. **Colour and Constitution.**—It was observed by Graebe and Liebermann (1868) that organic colouring matter on reduction gave colourless product which regained original colour on oxidation.

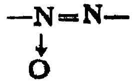
The relationship between colour and constitution was, however, pointed out for the first time in 1876 by the German chemist Otto Witt. He put forward his **chromophore auxochrome theory** of colour and constitution. According to him—

(*i*) Colour usually appeared in an organic compound when it contained certain *unsaturated groups* which should more appropriately be called *groups with multiple bonds.*

Witt called these groups with multiple bonds as **chromophores.** A few important chromophores are :



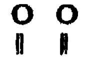
Nitro ;



$$\underset{\displaystyle O}{\overset{-N=N-}{\downarrow}}$$

Azoxy ; $-N=O$ Nitroso ; $-N=N-$ Azo

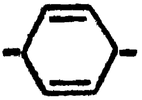
$C=O$; Carbonyl



$$-\overset{\displaystyle O}{\overset{\|}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-$$

Dicarbonyl ; $C=S$; Thiocarbonyl $-(HC=CH)_n-$ Polyene

and



(Quinonoid structure)

(*ii*) The compound containing the chromophoric group is called **chromogen.** It has been noticed that chromogens containing only one chromophore are usually yellow. Depth of the colour increases with the number of the chromophores.

A single C=C group as in ethylene ($CH_2=CH_2$) does not produce any colour. The colour, however, develops if a number of these groups are present in conjugation. For example, $CH_3—(CH=CH)_6—CH_3$ is yellow in colour.

(*iii*) Certain groups, which could not cause any colour effects in the absence of chromophore groups, do have an important effect on colour when they are introduced into a compound containing a chromophore group. Witt described such groups as
or colour augmenters or deepeners.

Some important auxochromes are :

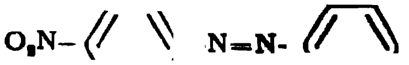
$-OH$; $-OR$; $-NH_2$; $-NHR$; $-NR_2$
Hydroxyl Alkoxy Amino Alkylated amino

Auxochromes are salt-forming groups and perform two functions :

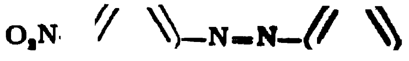
(*a*) They deepen the colour of the chromogen.

(*b*) Their presence is necessary to make the chromogen a dye.

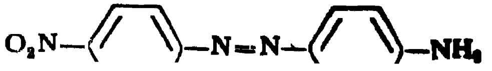
An interesting example of the effect of auxochrome groups may be noted with the following compounds :



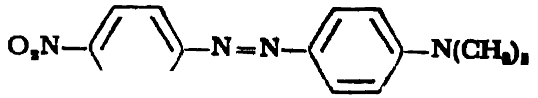
Red-orange



Deep yellow



Red-yellow



Deep red

The sulphonic and carboxyl groups possess little auxochromic properties but their presence makes the chromogen a dye. Presence of sulphonic group makes the dye soluble in water. Due to the presence of carboxyl group it forms lakes.

Numerous empirical observations have also been made. For example—

(*a*) Salts of phenols are more strongly coloured than free phenols.

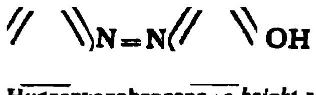
(*b*) Auxochromes do not affect the colour when present in the meta position to the chromophore.

Thus according to Witt's theory of colour and constitution :

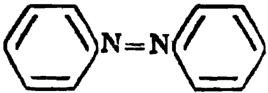
Chromogen = *A chromophore-bearing compound*, and

Dye = *Chromogen containing an auxochrome*.

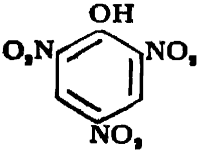
For example, in *p*-hydroxyazobenzene,



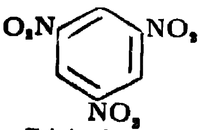
p-Hydroxyazobenzene (*a bright red dye*)

azobenzene,  is the chromogen, N=N is the chromophore and OH is an auxochrome.

Similarly, in picric acid (a yellow dye) trinitrobenzene is the chromogen containing three NO_2 groups (chromophores).



Picric acid
(*Dye*)



Trinitrobenzene
(*Chromogen*)

Here OH group is an auxochrome.

Some other terms introduced later are *bathochromic and hypsochromic groups*. The bathochromic groups bring about *deepening of colour in a dye* whereas the hyposchromic groups bring about the *lightening of colour*. The term deepening of colour in dye chemistry is being used for the following changes in colour :

Yellow → orange → red → purple → blue → green → black.

This is exactly the order of visible complementary colours of the colour absorbed with increase in the wavelengths of the absorbed light as given in the table on page 3·271. Hence we may say that longer the wavelengths of the absorbed light, deeper will be the colour of the dye.

Since visible colour is a complementary colour of the absorbed band, bathochromic groups (which bring about deepening of colour) will help absorption of longer wavelengths, *i.e.*, the colour absorbed will be one lying near the lower or red end of the column. *The bathochromic groups are, therefore, said to have a red shift.*

On the other hand, hypsochromic groups (which bring about lightening of colour) will help absorption of shorter wavelengths, *i.e.*, the colour absorbed will be one lying near the upper or blue end of the column. *The hypsochromic groups are, therefore, said to have a blue shift.*

4. Valence Bond Approach to Colour.—According to **Valence Bond Theory, the electron pairs of a molecule in its ground state are in a state of oscillation. When this molecule is placed in the**

path of a beam of light, it absorbs a photon of appropriate energy and gets excited and the amplitude of oscillation of its electron pair is increased. The wavelength of the photon absorbed depends on the energy difference between the excited and ground states of the molecule. The smaller the difference between the two states, the longer is the wavelength of the photon absorbed. It further states that—

(*i*) The energies of the both ground and excited states are lowered as a result of resonance among the charged structures.

(*ii*) Charged structures contribute more to the excited state than to the ground state.

(*iii*) The larger the number of electrons involved in resonance, the smaller is the energy difference between the excited state and the ground state.

Ethylene is colourless but a polyene is coloured. In fact, intensity of colour increases as the number of double bonds in a molecule increases. Let us understand this fact in the light of Valence Bond Theory.

Ethylene may be regarded as a resonance hybrid of (I) and (II).

$$\underset{\text{(I)}}{CH_2=CH_2} \longleftrightarrow \underset{\text{(II)}}{\overset{+}{C}H_2-\overset{-}{C}H_2}$$

Ground state of ethylene is represented predominantly by (I) and the excited state by (II). The energy difference between the two being very large, the energy of the photon required to excite ethylene is very high, *i.e.*, its wavelength is very short. The colour produced by absorption of these very short wavelengths will be very light.

In 1, 3-butadiene and 1, 3, 5-hexatriene there is greater contribution of charged structures to the resonance hybrid due to extended conjugation in these molecules. Since larger number of electrons are involved in resonance, the energy difference between the ground and excited states is smaller and longer wavelength of the photon is required to excite the molecule, *e.g.*,

$$CH_2=CH_2 \qquad CH_2=CH-CH=CH_2$$

*λ_{nm} 175 217

$$CH_2=CH-CH=CH-CH=CH_2$$

λ_{nm} 258

The longer the wavelength of the photon required for excitation, the greater the tendency for colour.

Presence of groups with +I/+R and/or −I/−R effect at the ends of the conjugated system will extend the conjugation as well as increase the contributions of charged structures to the resonance hybrid. As a result of it, the wavelengths of the photons required become longer as illustrated by the following examples :

Benzene is a resonance hybrid of two Kekule structures and a small amount of charged canonical structures (dipolar ions).

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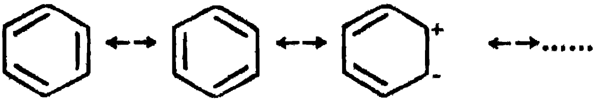
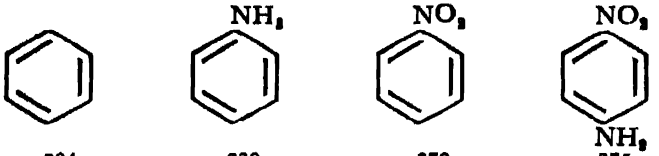
*λ_{nm} stands for wavelength in nanometres. 1 nm $= 10^{-9}$ metre.



Thus benzene itself is a chromophore. Presence of certain groups like NH_2, NO_2, etc., increases the wavelength of the photon required for excitation of the molecule, *e.g.*,



λ_{max} 204 230 270 375nm

Resonance in a conjugated system is maximum when the system is completely planar or almost so. If resonance is inhibited due to some steric effects, the depth of colour which depends on resonance will diminish and the compound may even become colourless.

5. **Classification of Dyes.**—Dyes are classified according to their chemical constitution or by their application to the fibre. The chemist prefers to classify dyes according to its structure but the dyer is mainly concerned with the reaction of dyes towards the fibre being dyed. Based on these two ways of classification, different forms of dyes have been described below :

ACCORDING TO APPLICATION

(1) **Direct or Substantive Dyes.** A compound is classified as a direct dye if it can be applied directly by immersing the animal and vegetable fibres or cloth in a hot solution of the dye in water.

Dyes suitable for dyeing animal fibres directly are subdivided into acid dyes and basic dyes.

(*a*) **Acid dyes** are sodium salts of sulphonic acid and nitrophenols and dye animal fibres (wool and silk) but not vegetable fibres. Wool and silk are dyed by dipping in their solution acidified with sulphuric or acetic acid.

(*b*) **Basic dyes** are the salts of colour bases with hydrochloric acid or zinc chloride. These dye animal fibres directly and vegetable fibres after these have been mordanted with tannin (*see under mordant dyes*). Basic dyes are mostly used for dyeing silk and cotton.

(2) **Mordant or Adjective dyes.** A mordant is any substance which can be fixed to the fibre and which can be dyed later on. Commonly used mordants are hydroxides or basic salts of chromium, aluminium or iron. Tannic acid is used as mordant with basic dyes. The fabric is mordanted by dipping in the solution of the metallic salt or tannin and then dipped into the solution of the dye when coloured lake is obtained which being insoluble is fast to washing. Alizarin and other anthraquinone dyes are applied in this way.

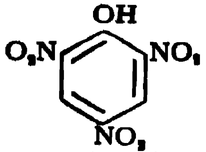
(3) **Ingrain Dyes.** These are dyes produced in the fibre itself during the process of dyeing. For example, a piece of cloth may be

soaked in an alkaline solution of β-naphthol and then dipped into a diazonium salt solution. Coupling takes place to produce an azo-dye in and on the fibre.

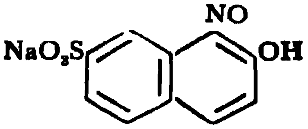
(4) **Vat Dyes**. These are water-insoluble coloured compounds which can be reduced to colourless (*leuco*) compounds which are soluble in alkali and readily reoxidised to the dye. After treatment in an alkaline bath the cloth is subjected to air oxidation which causes a return to the insoluble coloured form. Vat dyes in the leuco condition dye both animal and vegetable fibres directly but they are mostly used for cotton fibres. Indigo is an outstanding example of vat dye.

CLASSIFICATION BASED ON CHEMICAL STRUCTURE

(1) **Nitro and Nitroso Dyes**. These dyes are among the oldest synthetic dyes but are not important commercially. A few examples are :



Piric acid
(*Nitro dye*)



Naphthol Green B
(*Nitroso dye*)

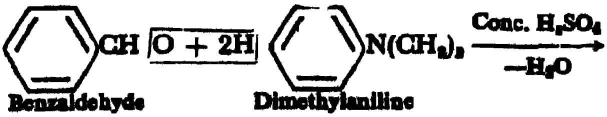
(2) **Triphenylmethane Dyes**. Triphenylmethane dyes have brilliant colours but they fade with washing and on exposure to light. These are used for colouring paper and typewriter ribbons.

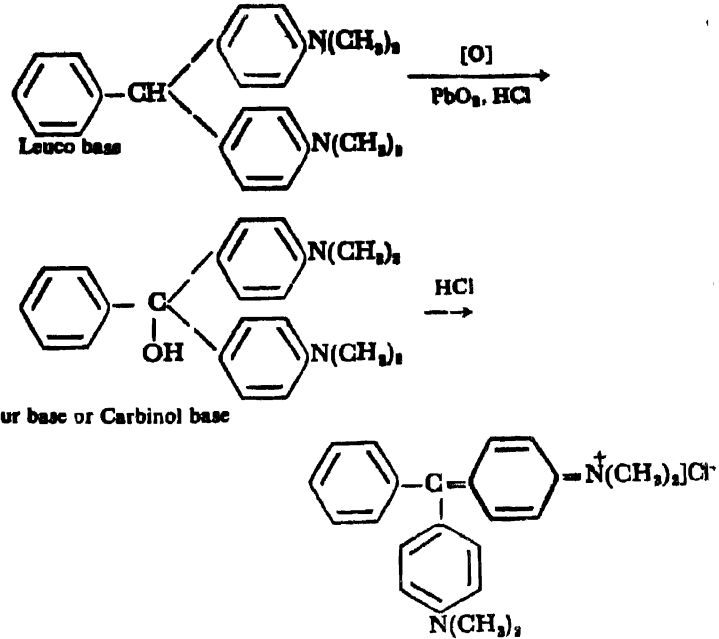
These dyes are obtained by introducing NH_2, NR_2, or OH groups (auxochromes) into the triphenylmethane ring (chromogen) when the colourless leuco compound is obtained. The leuco compound on oxidation gives the corresponding tertiary alcohol called the *colour base* (colourless benzenoid compound), which in presence of acid readily changes to the quinonoid *dye* due to salt formation. The changes are reversible.

$$\underset{\text{(Colourless)}}{\text{Leuco base}} \underset{\text{reduction}}{\overset{\text{oxidation}}{\rightleftharpoons}} \underset{\text{(Colourless)}}{\text{Colour base}} \underset{\text{alkali}}{\overset{\text{acid}}{\rightleftharpoons}} \underset{\text{(Coloured)}}{\text{Dye}}$$

Some important dyes of this class are :—

(*i*) **Malachite Green**. It is prepared by condensing benzaldehyde (1 molecule) with dimethylaniline (2 molecules) in presence of concentrated sulphuric acid followed by oxidation of leuco base with lead dioxide and hydrochloric acid to colour base which reacts further with hydrochloric acid to give malachite green.





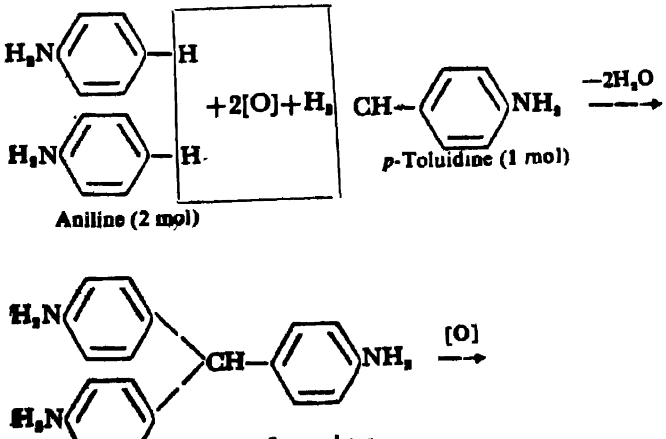
Leuco base

Colour base or Carbinol base

Malachite green

It dyes wool and silk directly and cotton after mordanting with tannin.

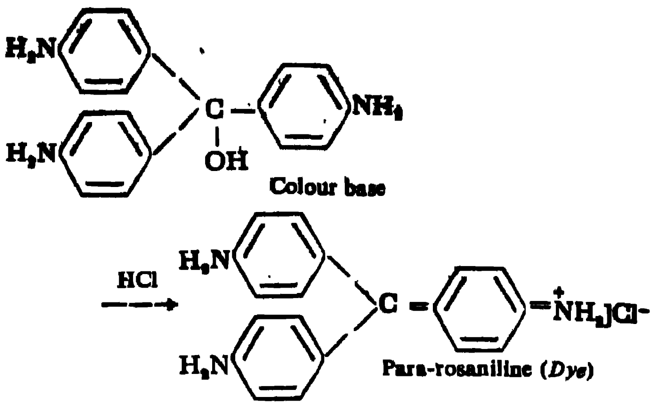
(ii) Para-rosaniline. It is prepared by oxidation of a mixtur of aniline (2 molecules) and *p*-toluidine (1 molecule) with nitrobenzene or arsenic acid.



Aniline (2 mol)

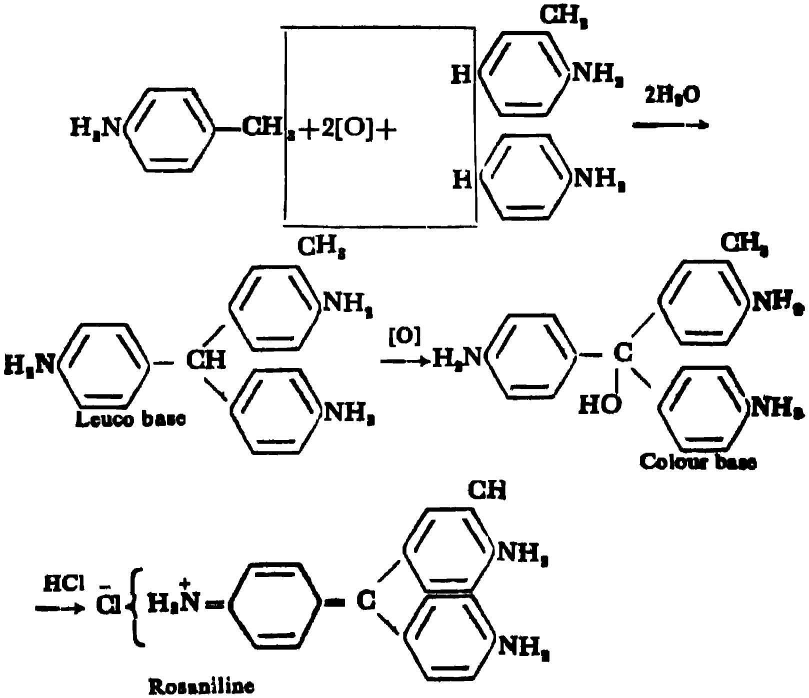
p-Toluidine (1 mol)

Leuco base



It dyes wool and silk directly and cotton after mordanting with tannin.

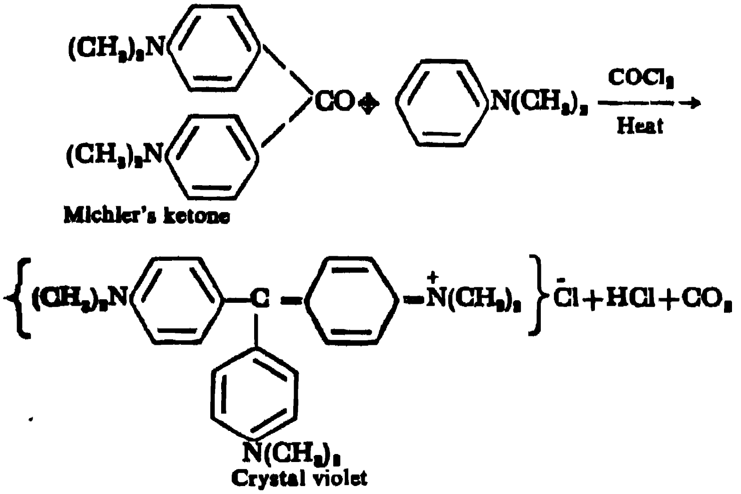
(*iii*) **Rosaniline, Fuchsine or Magenta.** It is *o*-methyl derivative of para-rosaniline and is prepared by oxidation of an equimolecular mixture of aniline, *o*- and *p*-toluidines with nitrobenzene in presence of iron filings. The product is a mixture of para-rosaniline and rosaniline in which the latter predominates.



Crystals of rosaniline show a green metallic lustre. It dissolves in water to give deep-red solution. The solution is decolorised by sulphur dioxide to get Schiff's reagent which gives a pink colour with aldehydes. The chemical changes involved in the preparation of Schiff's reagent are still uncertain.

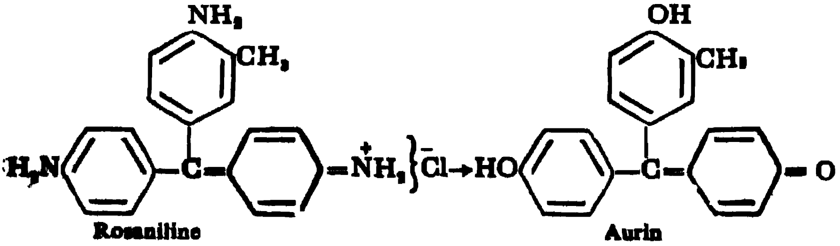
It dyes wool and silk directly and imparts violet-red colour. Cotton is dyed after mordanting with tannin.

(*iv*) **Crystal Violet.** It is prepared by heating Michler's ketone with dimethylaniline in presence of $POCl_3$ or $COCl_2$.



Bronzy-green crystals of the dye dissolve in water to give deep violet solutions. Wool and silk are dyed by it directly but cotton has to be mordanted before dyeing.

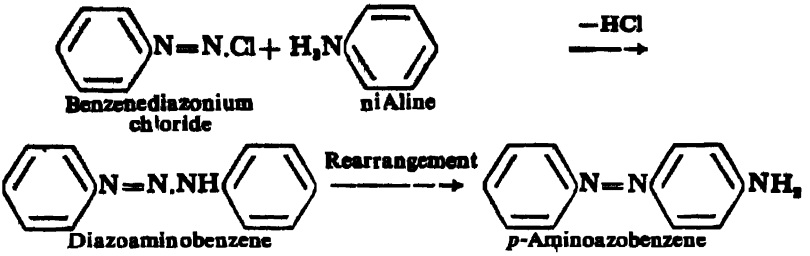
(*v*) **Aurin or Rosolic acid.** It is prepared by diazotising rosaniline and boiling the diazonium compound so obtained with water.



It is a crystalline solid crystallizing as red prisms which dissolve in alkalis to form intense red solution. It finds use as an indicator and printing wall papers.

(3) **Azo-dyes.** All azo-dyes have the same chromophore —N=N—, the azo-group whereas the auxochromes may be different. Common auxochromes are NH_2, NR_2 and OH groups. Some important members of this class of dyes are :

(*i*) **Aniline yellow** (*Aminoazobenzene*). It is prepared by coupling benzenediazonium chloride with aniline.



Benzenediazonium chloride

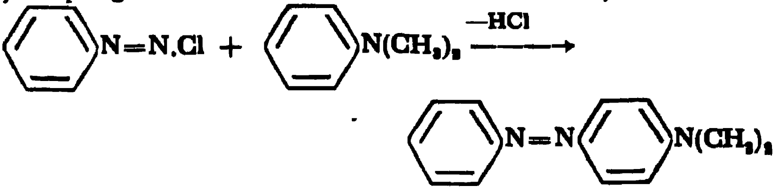
niAline

Diazoaminobenzene

p-Aminoazobenzene

It is the simplest basic azo-dye. Being sensitive to acids it is of very little value as a dye.

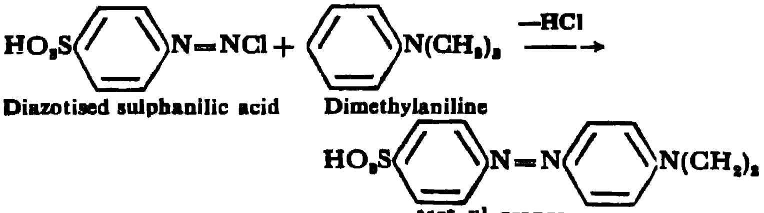
(*ii*) **Butter Yellow** (*p-dimethylamino-azobenzene*). It is obtained by coupling benzenediazonium chloride with dimethylaniline.



Butter yellow

Like aniline yellow it is a basic dye having very little value as dye.

(*iii*) **Methyl Orange.** It is prepared by coupling diazotised sulphanilic acid with dimethylaniline.

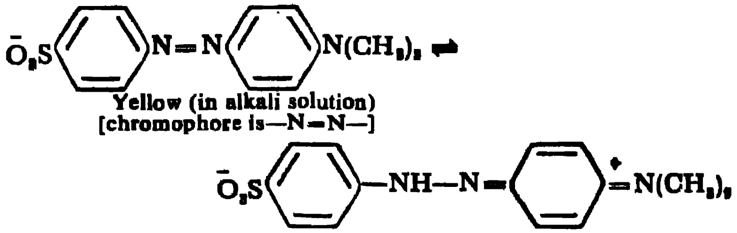


Diazotised sulphanilic acid

Dimethylaniline

Methyl orange

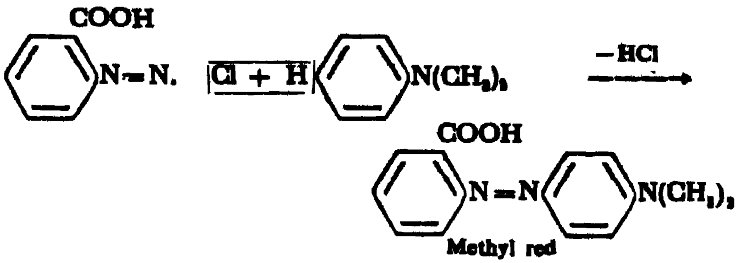
It is an acid dye. It dyes wool and silk and imparts them orange colour but the colour is not fast to light or washing. It is used as an indicator in acid alkali titrations as it gives yellow colour with alkali and pink with acid. The change in colour at the end point is due to the change in the structure of the ion.



Yellow (in alkali solution)
[chromophore is—N=N—]

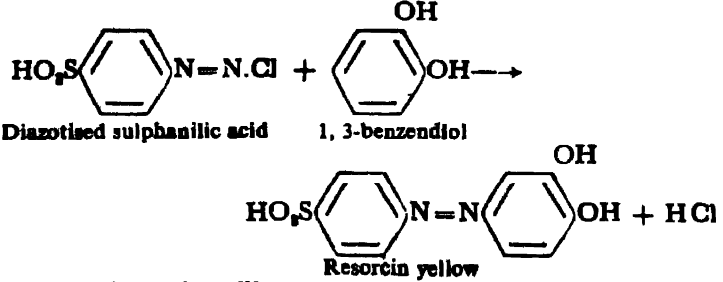
Pink (in acid solution)
[chromophore is *p*-quinonoid structure]

(*iv*) **Methyl Red.** This is another acid dye prepared by coupling diazotised *o*-aminobenzoic acid with dimethylaniline.



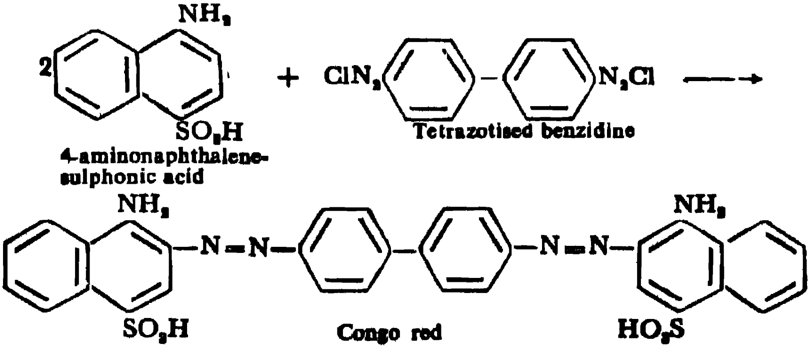
It is used as an indicator in acid-alkali titrations.

(*v*) **Resorcin Yellow.** It is a golden-yellow dye prepared by coupling diazotised sulphanilic acid with 1, 3-benzenediol.



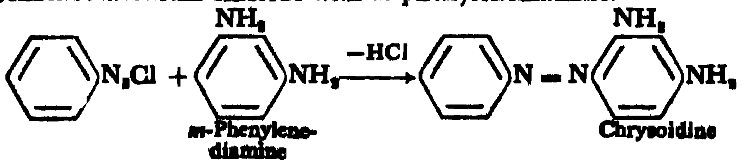
It is used in dyeing silk.

(*vi*) **Congo Red.** It is a dark red bisazo-dye prepared by coupling tetrazotised benzidine with two molecules of 4-aminonaphthalenesulphonic acid.



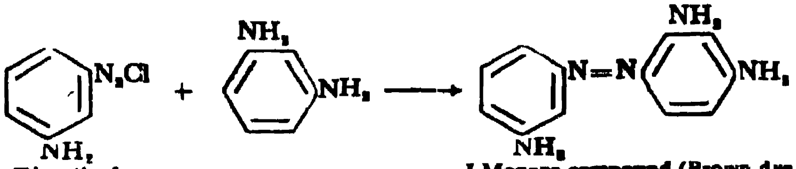
Its alkaline solution is red in colour which changes blue in presence of an acid. It is a direct dye used for dyeing cotton.

(*vii*) **Chrysoidine.** It is an orange-red dye obtained by coupling benzenediazonium chloride with *m*-phenylenediamine.



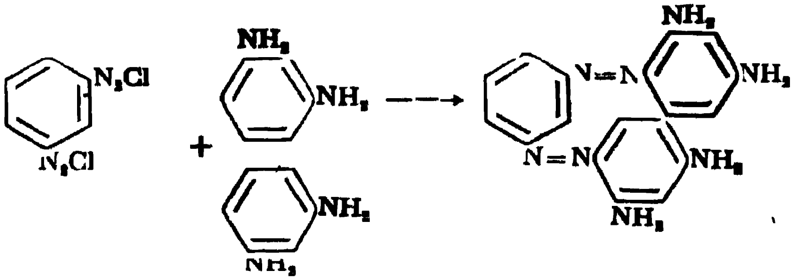
It is a direct dye used for dyeing wool and silk. For dyeing cotton the fabric has to be mordanted with tannin.

(*viii*) **Bismarck Brown.** It is a brown dye obtained by the action of nitrous acid on excess of *m*-phenylenediamine dissolved in concentrated hydrochloric acid. In fact it is a mixture of two dyes obtained by the diazotisation of one or both amino groups followed by coupling with the unchanged diamine.



Diazotised phenylenediamine

I Monoazo compound (Brown dye)



Tetrazotised benylenediamine

II Bisazo compound (Brown dye)

Bismarck Brown consists mainly of **II** with small amount of **I** It is used in boot polish and for staining wood before polishing. It is a direct dye for dyeing wool. For dyeing cotton it has to be mordanted before dyeing.

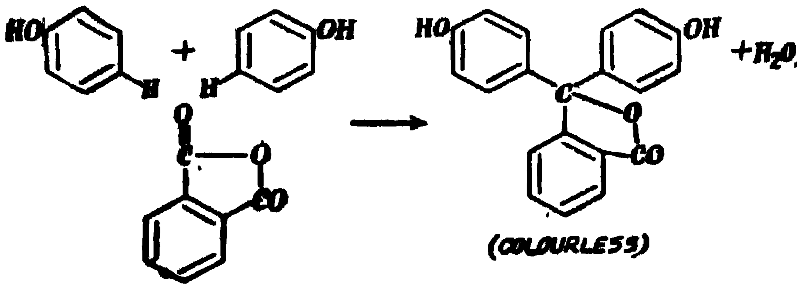
Structure Determination of Azo dyes. The structure of an azo-dye can be readily determined by its reduction with stannous chloride and hydrochloric acid or with sodium hyposulphite (dithionite). Reduction results in rupture of the azo group forming two primary amines which are then identified. From the structure of two primary amines we can assign a structure to the azo-dye.

$$\mathrm{Ar^1N{=}NAr^2} \xrightarrow{e^-\,;\,H^+} \mathrm{Ar^1NH_2 + Ar^2NH_2}$$

(4) **Phthaleins.** These are obtained by condensing phenols with phthalic anhydride in presence of some dehydrating agent like concentrated sulphuric acid or anhydrous zinc chloride. Some important members of this class of dyes are :

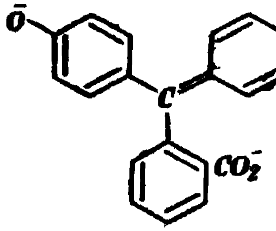
(*i*) **Phenolphthalein.** It is obtained by heating a mixture of phthalic anhydride (1 mol) and phenol (2 mol) with a concentrated sulphuric acid.

Phenol (*two molecules*)

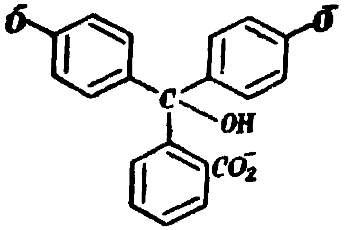


Phthalic anhydride

It is a white crystalline solid insoluble in water but soluble in alcohol. With alkalis it gives a pink colour which disappears on adding an acid. The change in colour is due to change in its structure as shown below :



Deep red

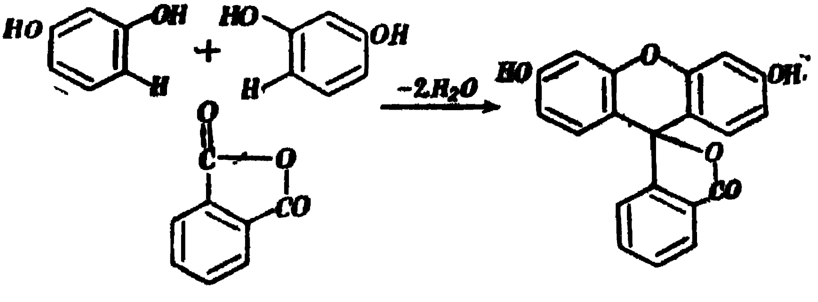


Colourless

It is used as an indicator

(ii) Fluorescein. It is obtained by heating a mixture of phthalic anhydride (*1 mol*) and *1, 3-benzenediol* (*2 mol*), concentrated sulphuric acid or anhydrous zinc chloride.

1, 3-benzenediol (*Two molecules*)



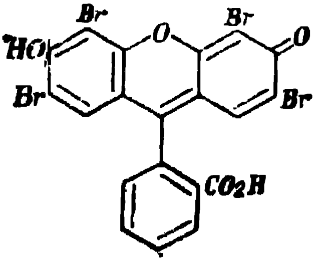
Phthalic anhydride **Fluorescein**

It is a red powder, insoluble in water. It dissolves in alkalis to give a reddish brown solution. On dilution the solution gives a strong yellowish green fluorescence.

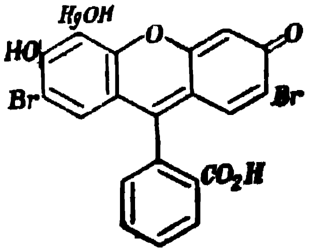
The sodium salt of fluorescein is known as **Uranine** which dyes wool and silk yellow from an acid bath.

(*iii*) **Eosin and Mercurochrome.** Eosin is prepared by bromination of fluorescein. It is a dye used for dyeing wool and silk or for preparing red ink.

Mercurochrome is obtained by mercuration of dibromofluorescein followed by treatment with caustic soda. It is an intense red dye. Its 2% solution is used as an antiseptic.



Eosin



Mercurochrome

QUESTIONS

Essay Type :

1. What is Witt's theory of colour and constitution ? Illustrate its application with reference to the use of phenolphthalein as an indicator in acid-alkali titrations. (*Delhi B.Sc. 1982, 77*)

2. Write a short note on Valence Bond Approach to colour. (*Delhi B.Sc. Hons. 1982*)

3. Explain the terms 'chromophore', 'chromogen' and 'auxochrome' What are bathochromic and hypsochromic groups ? What is meant by 'deepening of colour in dye chemistry ? Why are bathochromic groups said to have a red shift and hypsochromic groups a blue shift ?

4. Give one example each of the following :

(*a*) a mordant dye, (*b*) an azo dye, (*c*) a vat dye, and

(*d*) a triphenylmethane dye.

Indicate the synthesis of any one of them. (*Bangalore B.Sc.1974*)

5. What is a dye ? What are the requisites of a true dye ? How are they classified ? Mention a few important members of each class.

6. Give the preparation and uses of any four of the following :

(*i*) Fluorescein ; (*ii*) Congo red ; (*iii*) Malachite green ; (*iv*) Methyl orange ; (*v*) Phenolphthalein ; (*vi*) Bismarck brown ; (*vii*) Rosaniline ; (*viii*) Crystal violet. (*Rajasthan B.Sc. 1971*; *Madras 1971* ; *Kerala 1972* ; *Mysore 1972*)

7. Give an account of triphenylmethane dyes. (*Kerala B.Sc. 1973, 72*)

8. Write a short note on azo-dyes. (*Bombay B.Sc. Subsidiary 1971*)

9. (a) Give two examples each of 'chromophores' and 'auxochromes'. Explain briefly how the presence of chromophore gives rise to the potentiality of colour.

(b) Taking examples of ortho and para quinones, show that the colour is deeper, the greater is the resonance among the various charged forms.

(c) Give the preparation of methyl orange or phenolphthalein and explain the use of indicator in acid-base titrations. (*Delhi B.Sc. Hons. 1976*)

10. (a) Explain the terms 'direct' and 'indirect' dyes.

(b) Give the synthesis of any two of the following :

(i) Methyl orange, (ii) Alizarin and (iii) Indigo. (*Delhi B.Sc. Hons. 1975, 72*)

11. (a) Explain the term Leuco base, Colour base and a dye, giving suitable examples : (i) Congo Red ; (ii) Fluorescein. (*Delhi B.Sc. Hons. 1975, 73*)

12. Indicate the method of obtaining the following substances :

(i) Malachite green (ii) Phenolphthalein (iii) Alizarin (iv) Methyl orange. (*Delhi B Sc Hons. 1979*)

13. (a) Explain the terms . leuco base, colour base and a dye, giving a suitable example.

(b) Give the preparation of either methyl orange or phenolphthalein and explain the use of the indicator in acid-base titrations. (*Delhi B Sc Hons 1978*)

Short Answer Type :

1. An alcoholic solution of phenolphthalein is colourless but when a drop of alkali is added the solution becomes red in colour. Why ? (*Delhi B Sc. Hons. 1975*)

2. What are dyes ? What are the requisites of a true dye ?

3 What are chromophores ? Give five examples of chromophores

4. What is a chromogen ?

5. What are auxochromes ?

6. What is a mordant ?

7. What are ingrain dyes ?

8. What are vat dyes ? Give one example of a vat dye.

9. How are Leuco-base, colour base and a triphenylmethane dye related with one another ?

10 Write structures of methyl orange in alkali solution and acid solution.

11. How does the structure of phenolphthalein change as the solution changes from acidic to alkaline ?

12. What happens when aniline is treated with concentrated sulphuric acid at 450K ? Give the various steps leading to the preparation of methyl orange. (*Delhi B Sc. 1979*)

13. How would you obtain phthalic acid from naphthalene and convert it into fluorescein (*Delhi B Sc. 1979*)

14 Define the terms chromophore, auxochrome, bathochromic and hypsochromic. What role do these terms play in relation to Witt's theory of colour and constitution ? (*Delhi B Sc. 1979*)

15. How is the structure of an azo dye determined ?

Appendix I

PROBLEMS IN AROMATIC SYNTHESIS

1. **Introduction.**—From our study of the foregoing chapters, we have amassed a sizable knowledge of various aromatic substitution reactions. In various problems on aromatic synthesis we have to make use of this knowledge to synthesize a particular aromatic compound in as expeditious a manner as possible. For this purpose we must keep two kinds of information in mind.

(*i*) We must know all the different methods by which the given functional group could be introduced into the nucleus.

(*ii*) We must be aware of the directive influence of the group already present in the ring.

2. **Various Synthetic Routes.**—Various synthetic methods employed for introducing various substituents in an aromatic ring are summarized below :

(1) —**Cl**

(*i*) $ArH \xrightarrow[FeCl_3]{Cl_2} ArCl$ (Direct chlorination)

(*ii*) $ArNH_2 \xrightarrow{HNO_2} Ar\overset{\oplus}{N}_2 \xrightarrow{CuCl/HCl} ArCl$

(*Sandmeyer reaction*)

(2) —**Br**

(*i*) $ArH \xrightarrow[FeBr_3]{Br_2} ArBr$ (Direct bromination)

(*ii*) $ArNH_2 \xrightarrow{HNO_2} Ar\overset{\oplus}{N}_2 \xrightarrow{CuBr/HBr} ArBr$

(3) —**I**

$ArNH_2 \xrightarrow{HNO_2} Ar\overset{\oplus}{N}_2 \xrightarrow{KI} ArI$

(4) —**NO$_2$**

$ArH \xrightarrow[H_2SO_4]{HNO_3} ArNO_2$ (Nitration)

(5) —**NH$_2$**

(*i*) $ArNO_2 \xrightarrow[\text{or } (NH_4)_2S_x]{Sn + HCl} ArNH_2$

(*ii*) $ArCl \xrightarrow{NH_3} ArNH_2$

(To be used only if **Ar** is activated towards nucleophilic substitution by groups like NO$_2$ or COOH present in the ortho or para positions.)

(6) **—SO_3H**

$ArH \xrightarrow{SO_3/H_2SO_4} ArSO_3H$ (*Sulphonation*)

(7) **—COOH**

(*i*) $ArBr \xrightarrow{Mg} Ar\,MgBr \xrightarrow{CO_2} ArCOOH$

(*ii*) $ArCH_3 \xrightarrow{KMnO_4} ArCOOH$ (*Side chain oxidation*)

(*iii*) $ArCN \xrightarrow{H_3O^+} ArCOOH$ (*Hydrolysis*)

(*iv*) $ArCOCH_3 \xrightarrow{NaOCl} ArCOOH$ (*Haloform cleavage*)

(8) **—OH**

(*i*) $ArNH_2 \xrightarrow{HNO_2} Ar\overset{\oplus}{N}_2 \xrightarrow[H_2O]{H^+} ArOH$

(*ii*) $ArSO_3H \xrightarrow[\text{fusion}]{\text{NaOH (solid)}} ArOH$

(*iii*) $ArCl \xrightarrow{OH^-} ArOH$

(To be used only if **Ar** is activated as given under —NH_2 above.)

(9) **—C≡N**

$ArNH_2 \xrightarrow{HNO_2} Ar\overset{\oplus}{N}_2 \xrightarrow{K_3Cu(CN)_4} ArCN$

(10) **—COR**

$ArH \xrightarrow[AlCl_3]{RCOCl} ArCOR$

(Friedel-Crafts acylation reaction.)

(11) **R—**

$Ar\,H \xrightarrow[AlCl_3]{R-X} Ar-R$

(Friedel-Crafts alkylation reaction. Bear in mind rearrangement of R^+, if any.)

(12) **RCH_2—**

$ArH \xrightarrow[AlCl_3]{RCOCl} Ar\,COR \xrightarrow[HCl]{Zn(Hg)} ArCH_2R$

(Friedel-Crafts acylation + Clemmensen reduction)

(13) **—CHO**

$ArCOOH \xrightarrow{SOCl_2} ArCOCl \xrightarrow[\text{Xylene}]{Pd} ArCHO$

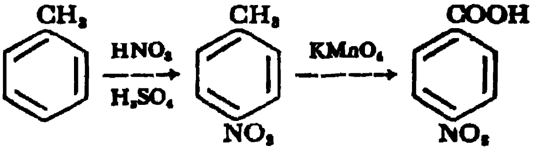
ArCOCl can also be reduced with lithium tri-*tert*-butoxyaluminium hydride, $LiAl[(CH_3)_3CO]_3H$

(14) —H

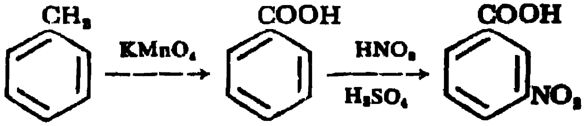
(*i*) $ArNH_2 \xrightarrow{HNO_2} \overset{\oplus}{ArN_2} \xrightarrow{H_3PO_2} ArH$

(*ii*) $ArSO_3H \xrightarrow{60\%H_2SO_4} ArH$

3. Sequence of steps.—The sequence of various steps involved in the synthesis will be governed by the directive influence of the various substituents present in the nucleus. For example, synthesis of *p*-nitrobenzoic acid from toluene involves the two steps : (*i*) nitration of toluene followed by (*ii*) oxidation of side chain.



The two reactions carried on in other sequence result in the formation of *m*-nitrobenzoic acid.



4. Some Typical Examples of Syntheses.

(1) **Conversion of Benzene into Toluene.** The conversion can be effected in two different ways as given below .

(*i*) $\underset{\text{Benzene}}{C_6H_5\boxed{H + Cl}CH_3} \xrightarrow[-HCl]{\text{Anhyd. }AlCl_3} \underset{\text{Toluene}}{C_6H_5.CH_3}$

(*ii*) $\underset{\text{Benzene}}{C_6H_6} \xrightarrow{Cl_2} \underset{\text{Chlorobenzene}}{C_6H_5Cl} \xrightarrow[-2NaCl]{+2Na+CH_3Cl} \underset{\text{Toluene}}{C_6H_5CH_3}$

(2) **Conversion of Toluene into Benzene.** Here again two methods are possible for the conversion as follows :

(*i*) $\underset{\text{Toluene}}{C_6H_5CH_3} \xrightarrow[KMnO_4]{[O]} \underset{\text{Benzoic acid}}{C_6H_5COOH} \xrightarrow[-CaCO_3]{\text{CaO, distil.}} \underset{\text{Benzene}}{C_6H_6}$

(*ii*) $\underset{\text{Toluene}}{C_6H_5CH_3} \xrightarrow[\text{hot and sunlight}]{Cl_2\text{ in}} \underset{\text{Benzylidyne chloride}}{C_6H_5CCl_3} \xrightarrow[-3HCl]{2H_2O} \underset{\text{Benzoic acid}}{C_6H_5COOH}$

$\xrightarrow{NaOH} C_6H_5COONa \xrightarrow[\text{dry heat}]{NaOH} \underset{\text{Benzene}}{C_6H_6} + Na_2CO_3$

(3) **Conversion of Phenol into**

$$\underset{\text{Phenol}}{C_6H_5OH} \xrightarrow[-ZnO]{\text{Zn dust, heat}} \underset{\text{Benzene}}{C_6H_6} \xrightarrow[\text{heat}]{CH_3Cl+\text{ anhy. }AlCl_3} \underset{\text{Toluene}}{C_6H_5.CH_3}$$

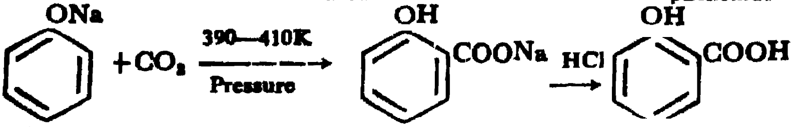
(4) **Conversion of Phenol into Benzoic acid**

$$\begin{tikzcd}
\underset{\text{Penol}}{C_6H_5OH} \arrow[r, "\text{Zn dust}", "-ZnO"'] & \underset{\text{Benzene}}{C_6H_6} \arrow[r, "\text{Conc. } H_2SO_4", "\text{heat}"'] & \underset{\text{Benzenesulphonic acid}}{C_6H_5SO_3H} \arrow[d, "KOH"] \\
\underset{\text{Benzoic acid}}{C_6H_5COOH} & \underset{\text{Phenyl cyanide}}{C_6H_5CN} \arrow[l, "+H_2O"', "-NH_3"] & \underset{\text{Pot. benzene-sulphonate}}{C_6H_5SO_3K} \arrow[l, "+KCN"', "\text{fuse}"]
\end{tikzcd}$$

(5) **Conversion of Toluene into *m*-chlorotoluene.** Toluene on direct chlorination gives *o*- and *p*-chlorotoluene. Hence an indirect method is used for preparing *m*-chlorotoluene as given on page 2·519.

(6) **Conversion of Benzene into Salicylic acid.**

$$\underset{\text{Benzene}}{C_6H_6} \xrightarrow{\text{Conc. } H_2SO_4} \underset{\text{Benzenesulphonic acid}}{C_6H_5SO_3H} \xrightarrow[\text{with NaOH}]{\text{Fused}} \underset{\text{Sodium phenoxide}}{C_6H_5ONa}$$



Sod. phenoxide Sod. salicylate Salicylic acid

QUESTIONS

1. **Starting from aniline how will you prepare the following:**
(*i*) Acetanilide, (*ii*) Phenyl isocyanide, (*iii*) Benzenediazonium chloride, (*iv*) Tribromoaniline, (*v*) *o*- and *p*-nitroaniline, (*vi*) Sulphanilic acid ?

2. How are the following conversions effected ?
(*a*) Benzene to Aniline, (*b*) Aniline to Phenol, (*c*) Benzene to Benzaldehyde, (*d*) Toluene to Benzoic acid ?

3. How are the following conversions effected ?
(*a*) Benzene to benzaldehyde, (*b*) Benzene to aniline, (*c*) Aniline to phenol, (*d*) Phenol to nitrobenzene.

4. Starting from benzene outline the synthesis of (*a*) Benzaldehyde, (*b*) Aniline, (*c*) Phenol, (*d*) Benzamide, (*e*) Benzyl chloride, and (*f*) *m*-nitroaniline.

5. **How will you synthesise :**
(*a*) Benzophenone from benzoic acid, (*b*) Salicylic acid from benzenesulphonic acid, (*c*) Nitrobenzene from aniline, (*d*) *p*-Amino-azobenzene, (*e*) Phenylhydrazine from benzamide, (*f*) Benzaldehyde from benzene.

6. **How will you synthesize :**
(*a*) *p*-isobutylbenzoic acid from benzene,
(*b*) 3,5-dibromotoluene from toluene ?

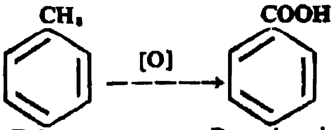
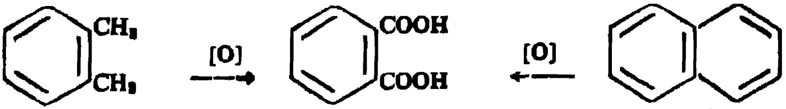
[**Hint.** Different steps involved are :
(*a*) (*i*) F-C reaction with $(CH_3)_2$ CHOOCl, (*ii*) Zn (Hg)+HCl, (*iii*) HNO_3, H_2SO_4, (*iv*) Sn, HCl, (*v*) HNO_2, (*vi*) $K_3Cu(CN)_4$, (*vii*) Hydrolysis.
(*b*) HNO_3, H_2SO_4 (*ii*) Sn, HCl (*iii*) Br_2, H_2 (*iv*) HNO_2, (*v*) H_3PO_2].

7. **Give the reagent(s) to bring about each of the following conversions.**
(*a*) Benzene to acetophenone, (*b*) Benzoic acid to bromobenzene,
(*c*) Benzene to benzaldehyde (*d*) Phenol to salicylaldehyde.
(*Osmania B.Sc. 1980*)

Appendix II

TYPICAL NUMERICAL PROBLEMS

1. **Problems on Structural Formula.**—Problems based on structural formula require a thorough knowledge of organic compounds and their reactions. Some important reactions commonly associated with unknown aromatic compounds and information given by them are summarized in the following table :

<table>
<tr><th>Reaction</th><th>Inference</th></tr>
<tr><td>(1) The compound on oxidation gives a new substance containing a new −COOH group.</td><td>The compound has a side-chain, <i>e.g.</i>,

Toluene Benzoic acid</td></tr>
<tr><td>(2) It gives phthalic acid on oxidation.</td><td>The compound has two side-chains (open or closed) in <i>o</i>-position, <i>e.g.</i>,</td></tr>
<tr><td colspan="2">
<i>o</i>-xylene (<i>containing two open side-chains</i>)
Phthalic acid
Naphthalene (<i>containing two closed side-chains</i>)</td></tr>
<tr><td>(3) It gives an addition product with bromine.</td><td>There is unsaturation in the side-chain, <i>e.g.</i>,</td></tr>
<tr><td colspan="2">$$\underset{\text{Styrene}}{C_6H_5.CH{=}CH_2} \xrightarrow{Br_2} \underset{\text{Addition product}}{C_6H_5CHBr.CH_2Br}$$</td></tr>
<tr><td>(4) Compound contains C, H and O.</td><td></td></tr>
<tr><td>(<i>a</i>) It gives a pink colour with Schiff's reagent.</td><td>It contains an aldehyde (−CHO) group.</td></tr>
<tr><td>(<i>b</i>) It gives a silver mirror with Tollen's reagent.</td><td>—Do—</td></tr>
<tr><td>(<i>c</i>) It gives an oxime with NH_2OH and phenylhydrazone with $C_6H_5NHNH_2$.</td><td>It contains a carbonyl group (aldehydic or ketonic).</td></tr>
<tr><td>(<i>i</i>) The above compound gives the reactions (<i>a</i>) and (<i>b</i>) above.</td><td>It is an aldehyde.</td></tr>
<tr><td>(<i>ii</i>) It does not give the reactions (<i>a</i>) and (<i>b</i>).</td><td>It is a ketone.</td></tr>
</table>

Reaction	Inference
(*d*) It gives one molecule each of an acid and an alcohol on treatment with KOH (*Cannizzaro* reaction).	Presence of —CHO group attached to the nucleus, *e.g.*,

$$\underset{\text{Benzaldehyde}}{2C_6H_5CHO} + KOH \longrightarrow \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + \underset{\text{Potassium benzoate}}{C_6H_5COOK}$$

Reaction	Inference
(*e*) It gives a coloration with $FeCl_3$.	Presence of phenolic group —OH group attached to the nucleus).
(*f*) It gives an effervescence with $NaHCO_3$ solution.	Presence of —COOH group.
(*g*) An aromatic acid loses water on heating.	The two carboxylic groups are in *o*-position as in phthalic acid.
(*h*) A dibasic acid with formula $C_6H_4(COOH)_2$ gives only one mono-nitro derivative.	It is tere-phthalic acid with two —COOH groups in *p*-position.

In general whenever a di-substituted compound gives only one tri-substituted derivative, it is p-derivative.

(5) Compounds containing C, H, N and O.

Reaction	Inference
(*a*) It gives NH_3 when heated with alkali.	Presence of $—CONH_2$ group, *e.g.*,

$$C_6H_5CONH_2 + NaOH \longrightarrow C_6H_5COONa + NH_3$$

Reaction	Inference
(*b*) Gives primary amine with Br_2 and KOH (*Hofmann Bromamide reaction*).	Presence of $—CONH_2$ group, *e.g.*,

$$\underset{\text{Benzamide}}{C_6H_5CONH_2} + Br_2 + 4KOH \longrightarrow \underset{\text{Aniline}}{C_6H_5NH_2} + 2KBr + K_2CO_3 + 2H_2O$$

Reaction	Inference
c) It gives an amine on hydrolysis.	Presence of (—NHCOR) group, *e.g.*

$$\underset{\text{Acetanilide}}{C_6H_5NH.\boxed{COCH_3 + NaO}H} \longrightarrow \underset{\text{Aniline}}{C_6H_5NH_2} + CH_3COONa$$

Reaction	Inference
(*d*) It is reduced by metal and acid to give an amine.	Presence of a nitro $(—NO_2)$ group.

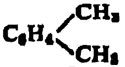
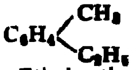
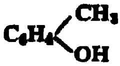
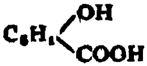
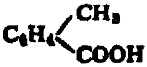
(6) Compounds containing C, H, and N only. Various possibilities are amines P, S and T, cyanides and isocyanides.

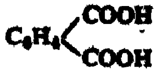
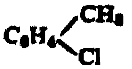
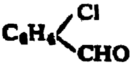
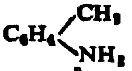
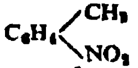
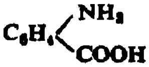
Reaction	Inference
(*a*) It is soluble in water and is alkaline towards litmus.	Presence of $—NH_2$ group in side-chain.
(*b*) It is soluble in dilute acid.	An amino-compound.
(*c*) It can be diazotised.	Presence of primary amino group attached to the nucleus.
(*d*) It gives an acid on hydrolysis and a primary amine on reduction.	It is a cyanide, *e.g.*,

$$\underset{\text{Primary amine}}{ArCH_2NH_2} \xleftarrow{4[H]} ArC\equiv N \xrightarrow{H_2O} \underset{\text{Acid}}{ArCOOH}$$

Reaction	Inference
(7) Compounds containing C, H and Cl.	
(*a*) It gives on oxidation an acid not containing chlorine.	Presence of —Cl in the side-chain, *e.g.*, benzyl chloride.
(*b*) It gives on oxidation a chloro-acid.	Presence of —Cl attached to nucleus, *e.g.*, chlorotoluene.
(*c*) Chlorine is easily replaced by —OH, $—NH_2$, — CN, etc.	Presence of —Cl in the side-chain.
(*d*) Chlorine is not easily replaced by these groups.	Presence of —Cl attached to the nucleus.

2. Isomeric Compounds.—A molecular formula might represent various isomers. Writing of possible isomers represented by a certain molecular formula is the first step. Later on we have to select one of these isomers which corresponds to the various reactions of the compound mentioned in the problem. Some important molecular formulae with possible isomers are given in the table below :

Molecular formulae	Various possible isomers		
(*i*) C_8H_{10}	 $C_6H_4\genfrac{}{}{0pt}{}{CH_3}{CH_3}$; *o*-, *m*- & *p*-xylenes (*three isomers*)	$C_6H_5C_2H_5$ Ethylbenzene	
(*ii*) C_9H_{12}	$C_6H_3(CH_3)_3$; Three isomeric trimethylbenzenes (*Adj* ; *unsym* ; *sym.*)	 $C_6H_4\genfrac{}{}{0pt}{}{CH_3}{C_2H_5}$ Ethylmethylbenzene	
	$C_6H_5.CH_2.C_2H_5$; *n*-propylbenzene	$C_6H_5CH(CH_3)_2$ Isopropylbenzene	
(*iii*) C_7H_8O	 $C_6H_4\genfrac{}{}{0pt}{}{CH_3}{OH}$; *o*-, *m*-, & *p*-methylphenols	$C_6H_5CH_2OH$; Benzyl alcohol	$C_6H_5O.CH_3$ Methoxybenzene
(*iv*) $C_7H_6O_3$	 $C_6H_4\genfrac{}{}{0pt}{}{OH}{COOH}$ *o*-, *m*- & *p*-Hydroxybenzoic acids		
(*v*) $C_8H_8O_2$	 $C_6H_4\genfrac{}{}{0pt}{}{CH_3}{COOH}$; *o*-, *m*- & *p*-Toluic acids	$C_6H_5.CH_2COOH$ Phenylacetic acid	

Molecular Formulae	Various possible isomers
(*vi*) $C_8H_6O_4$	 $C_6H_4{<}\begin{matrix}COOH\\COOH\end{matrix}$ *o*-, *m*- & *p*- Benzenedicarboxylic acids, Phthalic acid, isophthalic acid and *tere*-phthalic acid.
(*vii*) C_7H_7Cl	 $C_6H_4{<}\begin{matrix}CH_3\\Cl\end{matrix}$; $C_6H_5CH_2Cl$ Benzyl chloride *o*-, *m*- & *p*- chlorotoluenes
(*viii*) C_7H_5ClO	 $C_6H_4{<}\begin{matrix}Cl\\CHO\end{matrix}$; C_6H_5COCl Benzoyl chloride *o*-, *m*- & *p*- Chlorobenzaldehyde
(*ix*) C_7H_5N	$C_6H_5{-}C{\equiv}N$; Phenyl cyanide or Benzonitrile $C_6H_5{-}NC$ Phenyl isocyanide or Benzoisonitrile or carbylaminobenzene
(*x*) C_7H_9N	 $C_6H_4{<}\begin{matrix}CH_3\\NH_2\end{matrix}$; $C_6H_5NHCH_3$; *N*-Methylaniline; $C_6H_5CH_2NH_2$ Benzylamine *o*-, *m*- & *p*- Toluidine
(*xi*) $C_7H_7NO_2$	 $C_6H_4{<}\begin{matrix}CH_3\\NO_2\end{matrix}$; *o*-, *m*- & *p*- Nitrotoluenes $C_6H_5.CH_2N{<}\begin{matrix}\nearrow O\\ \searrow O\end{matrix}$ Phenylnitromethane $C_6H_5.CH_2{-}O{-}N{=}O$; Benzyl nitrite  $C_6H_4{<}\begin{matrix}NH_2\\COOH\end{matrix}$ *o*-, *m*- & *p*- Aminobenzoic acid

QUESTIONS

1. An organic monobasic acid when heated with soda lime gave an aromatic hydrocarbon of percentage composition C=91·303 and H=8·697 ; 0·9 g of its silver salt gave on ignition 0·4 g of silver. Find out its probable structure or structures. [*Poona B.Sc.* (*Part II*) *1971*]

2. An organic compound contains carbon=81·55% ; hydrogen=4·8% ; nitrogen=13·6% and has a vapour density=51·5. It evolves ammonia when heated with KOH, and on reduction with sodium and alcohol forms a base which reacts with HNO_2, giving off nitrogen and yielding alcohol. The alcohol can be oxidised to benzoic acid. What is the original organic compound ? Explain the above changes. [*Punjab TDC* (*III*) *1971*]

3. An organic compound A, having molecular formula C_9H_8, on chlorination in sunlight gives a product which on further hydrolysis furnishes a compound B. Treatment of B with acetic anhydride by the Perkin's reaction produces C which is an acid having a molecular weight of 148. Suggest graphic formulae with names, for compounds A, B and C. Discuss the reactions involved. (*Delhi B.Sc. 1971*)

4. An aromatic ketone X has the molecular formula $C_{12}H_{16}O_2$. On vigorous oxidation it yields a dibasic acid Y having the formula $C_9H_8O_5$ which rapidly forms an anhydride on heating. On strong heating with sodium hypobromite, it gives a monobasic acid Z, with the formula $C_9H_{10}O_3$. Z, when heated with soda lime, gives 3-methylanisole. Interpret the above reactions and deduce the structures of X, Y and Z. [*Delhi B.Sc.* (*Hons.*) *II year 1971*]

5. A compound R with molecular formula $C_9H_{10}O$ is insoluble in dilute acid and base. It does not reduce Tollen's reagent but forms a 2 : 4 dinitrophenylhydrazone. On vigorous oxidation it yields an acidic product $C_8H_6O_4$ which forms an acid anhydride upon heating. Treatment of R with sodium hypobromite gives a different acid which when heated with soda lime yields Toluene. Propose a structural formula for R. Explain the reactions involved. (*Delhi B.Sc. 1972*)

6. An aromatic monobasic acid A contains C=70·6%, H=5·88%. Its methyl ester has V.D.=75. When A is distilled with soda lime it gives a hydrocarbon. On oxidation with $KMnO_4$ it gives a monobasic acid B. Name the compound and four of its isomers? How will you distinguish between these isomers? Give equations for the reactions. (*Rajasthan B.Sc. 1971*)

7. Give structures of functional isomers of aromatic compounds whose molecular formula is C_7H_8O. How can you identify them? Describe preparation of any two of them. (*Rajasthan B.Sc. 1970*)

8. An organic dibasic acid A gave on analysis C=57·8%, H=3·6%. Its silver salt contained 56·8% Ag. On heating it forms a compound B [$C_8H_4O_3$] which reacts with $(NH_4)_2CO_3$ to form another compound C ($C_8H_5O_2N$). C forms potassium salt with alcoholic KOH, and forms compound D with alkaline NaClO. Compound D on dry distillation with soda lime forms aniline. Give structures of A, B, C and D and equations of reactions. (*Rajasthan B.Sc. 1970*)

9. Molecular formula of an organic compound A is $C_7H_5NO_4$. A on treatment with Sn/HCl gives a compound B whose molecular formula is $C_7H_7NO_2$. The compound B on treatment with $NaNO_2$/HCl at 0°C and subsequently boiling the reaction mixture gives a compound C. The molecular formula of compound C is $C_7H_6O_3$.

The compound C gives the following reactions:

(*a*) It gives a deep violet colour with alcoholic $FeCl_3$

(*b*) It evolves CO_2 from a solution of $NaHCO_3$

(*c*) It decomposes on heating to give phenol

Explain the above reactions with the help of equations and assign structures to the compounds A, B and C. (*Delhi B Sc Hons 1980*)

10. An aromatic ketone (A) having the empirical formula C_7H_6O reacted with hydroxylamine to yield a compound B with the molecular formula $C_{14}H_{13}O_2N$. On Beckmann rearrangement B gave an isomeric compound C which, on hydrolysis, yielded aniline and *p*-methoxybenzoic acid. Knowing that *anti*-rearrangements are common during Beckmann transformation, assign definite structures to A, B and C. Suggest a method for synthesis of A. [*Delhi B.Sc.* (*Hons.*) *1979*]

11. The aromatic base A, C_7H_9N forms a mono acetyl derivative B with acetic anhydride. Nitration with the nitrating mixture ($HNO_3+H_2SO_4$) converts B into a single product C, $C_9H_{10}O_3N_2$ which on hydrolysis, diazotization and reaction with cuprous bromide gives D, $C_7H_6O_2NBr$. Reduction of D with tin and concentrated hydrochloric acid yields another base E, C_7H_8NBr. Treatment of the diazonium salt of E with hypophosphorous acid gives bromotoluene.

Identify the substances A to E. [*Delhi B Sc.* (*Hons.*) *1970*]

12. On ozonolysis $C_{18}H_{20}O$ (X) gives $C_{10}H_{12}O$ (A) and $C_8H_8O_2$ (B). A gives the iodoform reaction and with NH_2OH gives the oxime $C_{10}H_{13}ON$ (C). The oxime with PCl_5 in dry ether gives an amide which can be hydrolyzed to CH_3COOH and a compound, $C_8H_{11}N$ (D). D with HNO_2 at 0°C gives an aromatic alcohol, $C_8H_{10}O$, oxidation of which gives phthalic acid. B on mild oxidation gives a carboxylic acid, $C_8H_8O_3$, which is degraded by HI to CH_3I and *p*-hydroxy benzoic acid. Identify the compound (X) and give the reaction sequence involved. [*Delhi B.Sc.* (*Hons.*) *1971*]

13. Compound A of formula C_7H_9N dissolves readily in dilute hydrochloric acid. When this solution was cooled, treated with sodium nitrite and then with an alkaline solution of 2-naphthol, a red solid separated. When A was treated with bromine water solid B precipitated immediately. Quantitative analysis showed that B contained 70·0% bromine.

(*a*) What is molecular formula of B ?

(*b*) What was the structure of A ? (*Allahabad B.Sc. 1971*)

14. A hydrocarbon C_9H_{10} (A) rapidly decolorises cold aqueous permanganate and readily absorbs one molecule of bromine. Vigorous hydrogenation of (A) gives a compound (B) of the formula C_9H_{16}. Strong oxidation of (A) yields phthalic acid. Propose a structure for (A) and give the basis for your answer. (*Allahabad B.Sc. 1970*)

15. An aromatic organic compound A has the molecular formula $C_9H_{11}O_2N$. On hydrolysis with dilute sulphuric acid A gives one molecule of B plus one molecule of acetic acid. B on diazotisation and treating with large excess of dilute sulphuric acid at 100°C gives C. C when treated with strong hydriodic acid yields methyl iodide and compound D. Oxidation with acid dichromate converts D into E which is not aromatic in nature. B can form only two mono-nitro derivatives. Deduce the structures of the compounds A to E and give the sequence of reactions. (*Delhi B.Sc. Hons. 1979*)

16. An aromatic hydrocarbon A containing 90·6% carbon on oxidation gave a dicarboxylic acid B which when nitrated, forms only one mononitro derivative C. Deduce the structures of A, B and C. (*Rajasthan B.Sc. 1975*)

17. An aromatic compound is found to have the molecular formula $C_7H_7O_2N$. Write the structural formulae of the different isomeric compounds represented by this molecular formula. How can these compounds be distinguished from one another ? (*Rajasthan B.Sc. 1974*)

18 An organic compound A contains C=92·3% and H=7·7%. Its vapour density has been found to be 52. A is oxidised by $KMnO_4$ solution in cold and when fully oxidised, gives an acid B which contains C=68·8% and H=4·9%. A reacts with bromine and gives a compound C containing 60·6% bromine. What is the structure of A ? (*Rajasthan B.Sc. 1973*)

19. An aromatic compound (A) contains C=68·85%, H=4·92%. Its vapour density is 61 and it forms bisulphite compound. (A) reacts with conc. NaOH solution to give two compounds (B) and (M). (B) contains C=60·94%, H=4·3% and can be obtained by the oxidation of (A). (B) on distillation with sodalime gave phenol and gives violet colour with $FeCl_3$. (M) contains C=67·75%, H=6·45% and can be obtained by reducing (A). What are (A), (B) and (M) ? Write their structural formulae and explain the above reactions. (*Rajasthan B.Sc. 1972*)

20. A neutral compound [A] C_7H_6O forms an oxime. When [A] is treated with acetic anhydride and sodium acetate yields a product [B] which decolorises alkaline $KMnO_4$ solution and also gives effervescence with $NaHCO_3$. Explain the reaction and assign structures to A and B. (*Osmania B.Sc. 1980*)

21. (*a*) Compound A of formula $C_9H_{12}O$ responded to a series of tests as follows :

(*i*) Na → slow formation of H_2 gas bubbles.

(*ii*) acetic anhydride → pleasant smelling product.

(*iii*) hot $KMnO_4$ → benzoic acid.

(*iv*) Br_2/CCl_4 → no decolorization.

(*v*) I_2+NaOH → pale yellow solid, m.p. 392K (iodoform).

(*vi*) rotated plane-polarized light.

What was A ? Write equations for all the above reactions.

(*b*) Compound B, an isomer of A, was also found to be optically active. It showed the same behaviour as A except for test (*v*). From the careful oxidation of B by $KMnO_4$, there was isolated an acid of formula $C_9H_{10}O_2$. What was B ? (*Bombay B.Sc. Principal 1972*)

22. A white solid A of the molecular formula $C_{13}H_{10}OClN$, on reaction with phosphorus pentachloride in ether at 273K, gives a compound B which may be hydrolysed to equimolar quantities of p-chloroaniline and benzoic acid. What structure would you assign to A? (*Delhi B.Sc. Hons. 1976*)

23. Compounds A and B are isomers having the molecular formula C_8H_{10}. On oxidation A gives benzoic acid while B gives phthalic acid which forms an anhydride C on heating. Write down the names and structural formulae of A, B and C. Explain the reactions involved. (*Delhi B.Sc. 1976*)

24. An organic compound A has the molecular formula C_8H_{10}. On oxidation, it gives a dibasic acid B with the molecular formula $C_8H_6O_4$. On heating, the acid B was converted into another compound C having the formula $C_8H_4O_3$. The acid B on distillation with soda-lime gave the hydrocarbon C_6H_6. What structural formulae would you assign to A, B and C? Give the equations of the reactions involved. (*Delhi B.Sc. Hons. 1976*)

25. An organic compound (A) $C_7H_6O_2$ forms a crystalline derivative with sodium bisulphite. When (A) is treated with cold sodium hydroxide solution, two substances, the sodium salt of an acid (B) and (C) a primary alcohol are obtained. (B) which contains C=60·9% and H=4·35%, may also be obtained by oxidation of (A). (B) when distilled with soda-lime gives phenol. (C) which contains C=67·75% and H=6·45% may be obtained by reducing (A). Explain all the reactions and give structural formulae of A, B and C. (*Gorakhpur B.Sc. 1971*)

26. A hydrocarbon (A) having the molecular formula C_8H_{10} on oxidation gives a dicarboxylic acid (B) which on nitration forms only one mononitro compound. Write the structures of A and B. (*Gorakhpur B.Sc. 1972*)

27. An aromatic hydrocarbon (A) containing 91·3% carbon gives on chlorination three isomeric monochloro derivatives X, Y and Z. Percentage of chlorine in each one of these is 28. On oxidation with potassium permanganate all the three give one monobasic acid. Acid obtained from X gives benzene on distillation with soda-lime. Acids obtained from Y and Z on similar treatment give monochlorobenzene. Determine the structural formulae of various compounds. Explain the reactions involved. (*Gorakhpur B.Sc. 1973*)

28. An organic compound A containing 69·40% C, 5·83% H and 11·56% N was subjected to Hofmann degradation (treated with sodium hypobromite and heated). The resulting compound B was purified by steam distillation. Compound B contained 77·38% C, 7·58% H and 15·04% N. When it was heated with acetic anhydride, a crystalline compound C containing 71·09% C, 6·71% H and 10·36% N was obtained. Find out the molecular formula of A, B and C and describe the chemical transformations involved by the equations. (*Madras B.Sc. 1972 Sept.*)

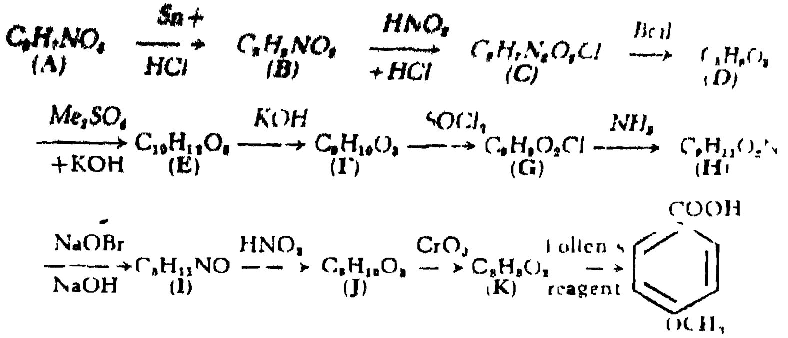
29. A monoterpenoid A containing 78·89% C, 10·59% H was oxidised with HNO_3 to give a compound B with the same number of carbon atoms containing 59·98% C and 8·05% H. The equivalent weight of B was found to be 100 by the silver salt method. Find out the molecular formulae of A and B and describe by an equation the chemical transformation of A to B. (*Madras B.Sc. 1972 April*)

30. A compound (A) of the formula $C_7H_3O_4NCl_2$ is soluble in alkali. The compound on reduction with iron and hydrochloric acid followed by

[illegible]

(Gauhati B.Sc. Hons. 19[illegible])

31. Outline the reactions as shown below and name the products formed in each case :



(Calcutta B.Sc. Hons. 1974)

[Hint. Start working back from the final product to get K then J → I → H → G → F → E → D → C → B → A.]

32. An organic compound A ($C_8H_{14}O$) forms an oxime and gives a positive haloform reaction. On ozonolysis, it gives acetone and a compound B ($C_5H_8O_2$). B forms a dioxime and on subjecting to haloform reaction gives an acid C ($C_4H_6O_4$). On treatment with excess of ammonia and strong heating C gives a neutral compound D ($C_4H_5O_2N$). D on distillation with zinc dust forms pyrrole. Suggest possible structures of A, B, C and D. Explain the chemical reactions involved. *(Delhi B.Sc. Hons., 1976)*

33. An aromatic organic compound A gave a solid crystalline product with $NaHSO_3$. With a saturated solution of sodium hydroxide it gave a compound B and the sodium salt of an aromatic monobasic acid C. The compound B has 77·8% carbon and 7·4% hydrogen. C on distillation with soda-lime gave benzene. B on oxidation with potassium permanganate gave C. Give the names and structural formulae of A, B and C. Write down the reactions involved.

(Delhi B.Sc. 1977 Supp.)

34. An organic compound (A) having the molecular formula $C_5H_{10}O$ gives a precipitate with dinitrophenylhydrazine. Iodine in the presence of aqueous sodium carbonate reacts with (A) to give iodoform. Reduction of (A) gives (B), $C_5H_{12}O$. When heated with concentrated sulphuric acid, compound (B) yields (C), C_5H_{10}. Ozonolysis of (C) gives two compounds (D), C_2H_4O and (E), C_3H_6O. Identify the compounds (A), (B), (C), (D) and (E), giving reasons. Explain the reaction of aqueous alkali on (D) and (E). *(Delhi B.Sc. Hons. 1978)*

35. A compound A contains 66·4% carbon, 5·53% hydrogen and 28·05% chlorine. When it is oxidised with $KMnO_4$ an acid B containing 68·8% carbon, 4·9% hydrogen is produced. When A is treated with NaOH, M is produced which contains 77·8% carbon and 7·4% hydrogen. Explain these reactions. Give the structures of isomers of A and show how they differ from A.

(Delhi B.Sc. 1982)

36. An organic monobasic acid contains carbon 60·87% and hydrogen 4·35%. Its silver salt contains 44·05% of silver. When the acid is distilled with soda-lime a characteristic smelling substance is obtained which gives violet colour with ferric chloride solution.

In a separate experiment the acid on reduction gives another acid which on distillation with soda-lime gives benzene.

Explain these reactions and assign the structural formula to both the acids. *(Ravi Shanker B.Sc. 1972)*

37. A polycyclic aromatic hydrocarbon (A), containing 94·34% C and 5·66% H, is oxidised with chromium trioxide carefully to yield a compound (B), having 80·76% C and 3·87% H. On further oxidation with hydrogen peroxide, (B) gave an acid having 69·42% C and 4·16% H. Describe the chemical transformations involved by means of equations. *(Madras B.Sc. 1973)*

38 A substance (A) of the molecular formula $C_{12}H_{11}O$ reacts with hydroxylamine to furnish a compound (B), having the molecular formula $C_{12}H_{11}ON$. (B) is converted by the action of phosphorus pentachloride into an isomeric compound (C). When hydrolysed with alkali, the compound (C) gives 2-naphthylamine. Deduce the structures of (A), (B) and (C). *(Calicut B.Sc. 1972)*

39 An organic compound A (C_7H_7Cl) gives two isomeric mononitro derivatives B and C. 'A' does not give a precipitate with alcoholic $AgNO_3$ but on oxidation with $KMnO_4$ gives D ($C_7H_5O_2Cl$) which on heating with soda-lime gives C_6H_5Cl. On treatment with $NaNH_2$ 'A' gives a mixture of the isomeric compounds E and F of formula C_7H_9N. Both E and F can be diazotised and coupled with 2-naphthol E but not F on diazotisation and warming with CuCl gives back A Give structures for the compounds and explain the formation of E and F from A. *(Madras B.Sc. 1980)*

40. An organic compound A, having the molecular formula $C_{13}H_{10}O$, can be synthesised from benzene and benzoyl chloride in presence of anhydrous aluminium chloride. Compound A reacts with hydroxylamine to form a derivative B (Molar formula $C_{13}H_{11}ON$). On heating the compound B with sulphuric acid a rearrangement occurs and a compound C is obtained. On prolonged heating with aqueous NaOH compound C gives a liquid D (Molar formula C_6H_7N) which is collected by steam distillation. When an acidic solution of D is chilled and treated with $NaNO_2$ and then with 2-naphthol, a red dye is obtained.

Explain the above reactions with the help of equations and assign structure to the compounds A, B, C and D. *(Delhi B.Sc. Hons. 1981)*

41 An organic compound A whose vapour density is 64, contains 93·75% carbon and 6·25% hydrogen. A on catalytic oxidation gave B containing 64·86% carbon, 2·7% hydrogen and 32·34% oxygen. B on hydrolysis gave an acid C which is dicarboxylic in nature (Equivalent weight=83). C on heating with soda-lime yielded a hydrocarbon containing 92·3% carbon. Identify A, B and C. *(Kamraj University B.Sc. 1981)*

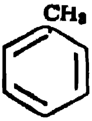
42. An aromatic liquid of molecular formula C_7H_8O reacts with metallic sodium liberating hydrogen gas Oxidation of A at first gives a colourless oily liquid B of molecular formula C_7H_6O. Prolonged oxidation of A gives finally a white crystalline solid C of molecular formula $C_7H_6O_2$. C dissolves in sodium hydroxide solution to give compound D of molecular formula $C_7H_5O_2Na$. When D is strongly heated with soda-lime, benzene is formed. Identify compounds A, B, C, and D. Explain the reactions involved. *(Madras B.Sc. 1980)*

43. A neutral organic substance A of molecular fomula $C_{13}H_{10}O_2$ on boiling with alkali gives B ($C_7H_6O_2$) and C (C_6H_6O). B is soluble both in NaOH and in $NaHCO_3$ and on heating with alcohol in presence of anhydrous zinc chloride gives a pleasant smelling liquid D ($C_9H_{10}O_2$). C is soluble in NaOH but insoluble in $NaHCO_3$. On heating with chloroform and alkali it gives E ($C_7H_6O_2$) which gives a silver mirror with Tollen's reagent and blue colour with ferric chloride. E on oxidation gives F ($C_7H_6O_3$) which is soluble in $NaHCO_3$ and gives a violet colour with ferric chloride. Write the structures of the compounds A to F and explain the reactions involved. *(Madras B. Sc. 1980)*

44. An organic compound A contains C=81·55%, H=4·8% and N=13·6%. Its vapour density is 51·5. It evolves NH_3 when hydrolysed with KOH and gives B. A on reduction with sodium and alcohol gives a base C. C reacts with HNO_2 giving off N_2 and yields an alcohol D. The alcohol on oxidation gives benzoic acid. Identify A, B, C, and D and explain all the reactions. (*Indore B.Sc. 1981*)

ANSWERS

1. Hydrocarbon C_7H_8, probable structure



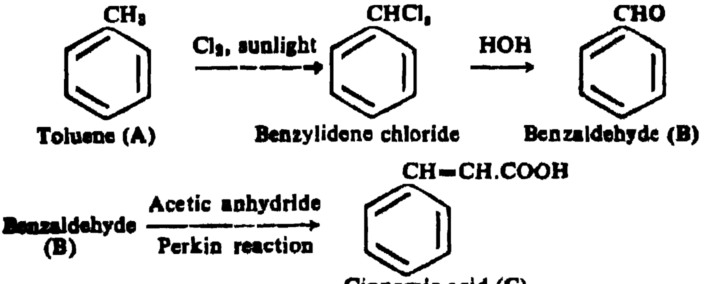
2.

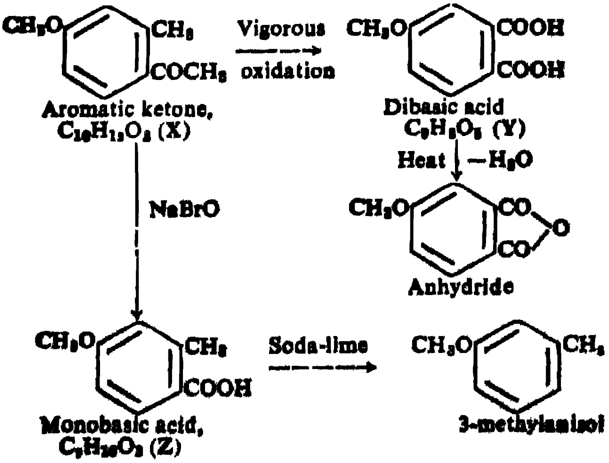
$$\underset{\text{Phenyl cyanide or Benzonitrile}}{C_6H_5CN} \xrightarrow[4H]{\text{Na and alcohol}} \underset{\text{Benzylamine}}{C_6H_5CH_2NH_2}$$

$$C_6H_5CN \xrightarrow{\text{Heat, KOH}} \underset{\text{Potassium benzoate}}{C_6H_5COOK} \ (+NH_3)$$

$$C_6H_5CH_2NH_2 \xrightarrow{HNO_2} \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} \xrightarrow{O} \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

3.





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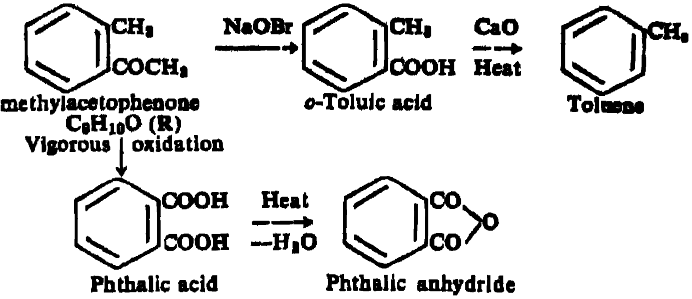

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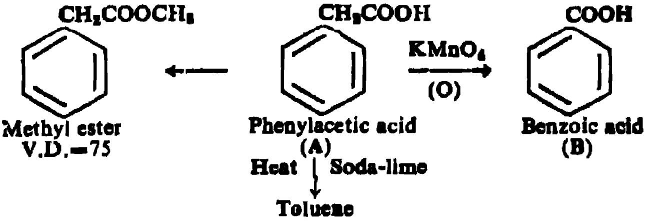
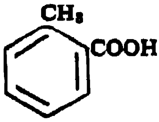
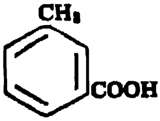


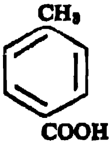
Isomers :



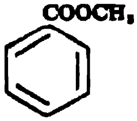
o-toluic acid ;



m-toluic acid ;

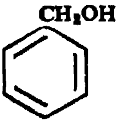


p-toluic acid ;

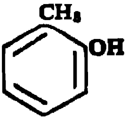


Methyl benzoate

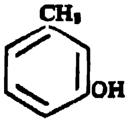
7.



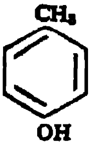
Benzyl alcohol ;



o-methylphenol

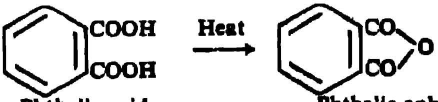


m-methylphenol ;

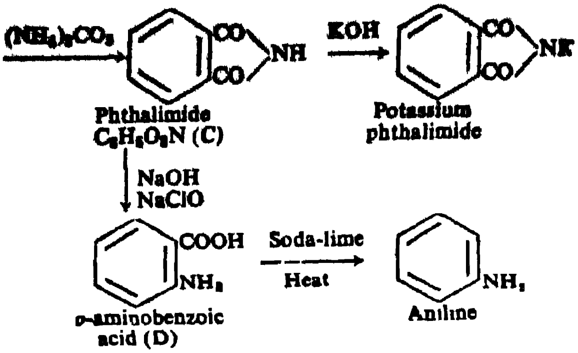


p-methylphenol

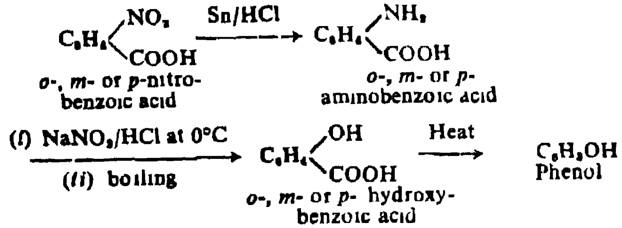
8.



Phthalic acid (A) Phthalic anhydride $C_8H_4O_3$ (B)



9.



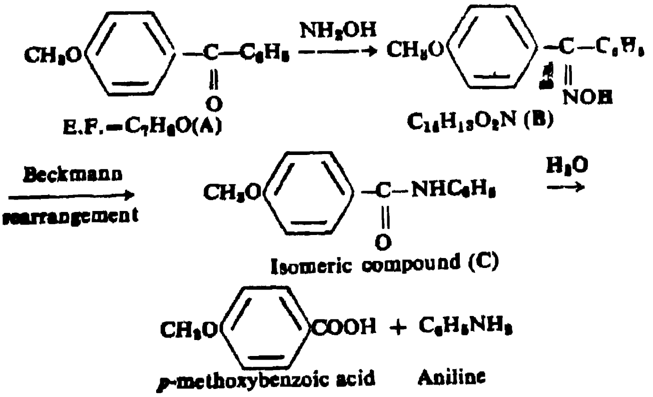
$$C_6H_4\begin{matrix}NO_2\\COOH\end{matrix} \xrightarrow{Sn/HCl} C_6H_4\begin{matrix}NH_2\\COOH\end{matrix}$$

o-, m- or p-nitrobenzoic acid → o-, m- or p-aminobenzoic acid

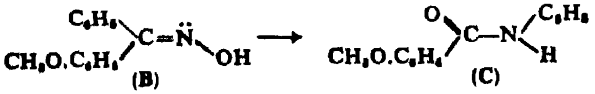
$$\xrightarrow[(ii)\ \text{boiling}]{(i)\ NaNO_2/HCl\ \text{at}\ 0°C} C_6H_4\begin{matrix}OH\\COOH\end{matrix} \xrightarrow{\text{Heat}} C_6H_5OH$$

o-, m- or p-hydroxybenzoic acid; Phenol

10.

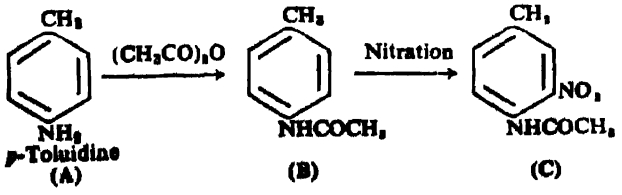


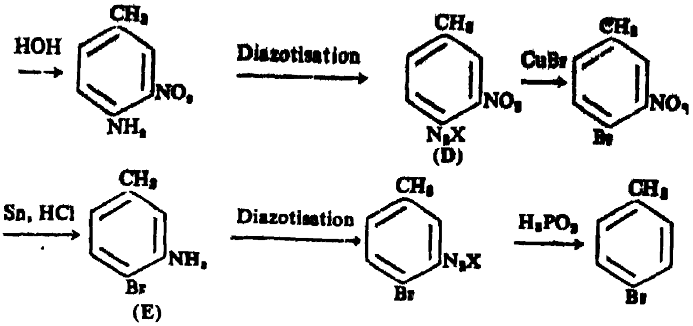
Stereochemical arrangement of Aryl group :



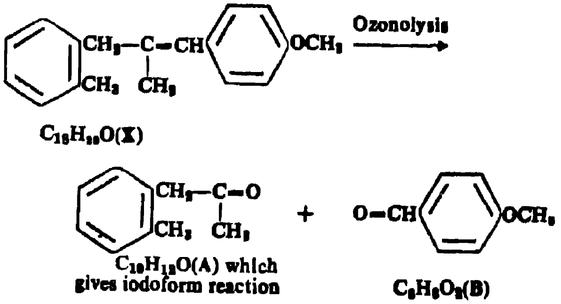
It is C_6H_5 group *anti* to the OH group in B, that migrates from C to N atom.

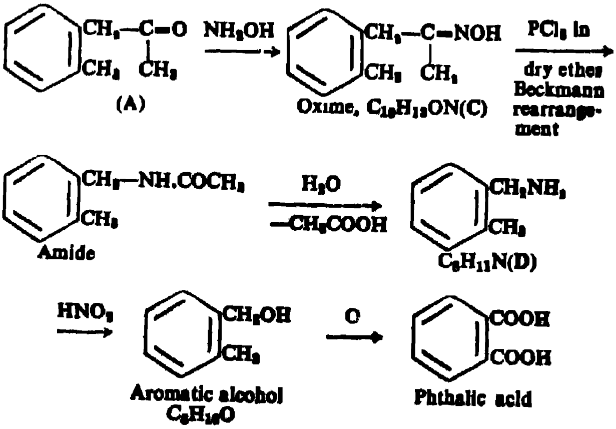
11.

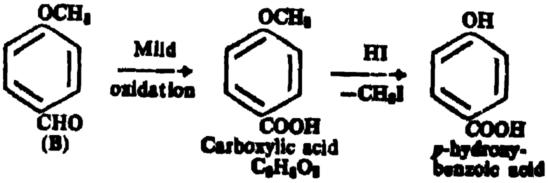



HOH
CH3
NO2
NH2
Diazotisation
CH3
NO2
N2X
(D)
CuBr
CH3
NO2
Br
Sn, HCl
CH3
NH2
Br
(E)
Diazotisation
CH3
N2X
Br
H3PO2
CH3
Br

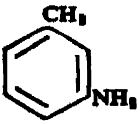
12.


CH2—C=CH
CH3 CH3
OCH3
Ozonolysis
C18H20O(X)
CH2—C=O
CH3 CH3
+
O=CH
OCH3
C10H12O(A) which gives iodoform reaction
C8H8O2(B)

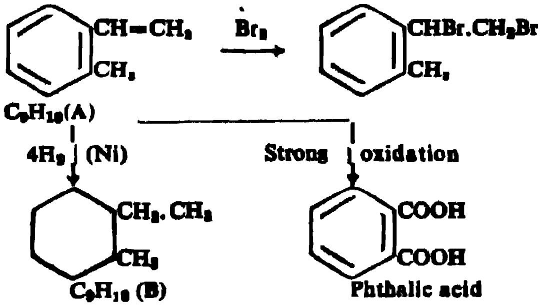

CH2—C=O
CH3 CH3
(A)
NH2OH
CH2—C=NOH
CH3 CH3
Oxime, C10H13ON(C)
PCl5 in dry ether Beckmann rearrangement
CH2—NH.COCH3
CH3
Amide
H2O
—CH3COOH
CH2NH2
CH3
C8H11N(D)
HNO2
CH2OH
CH3
Aromatic alcohol C8H10O
O
COOH
COOH
Phthalic acid


OCH3
CHO
(B)
Mild oxidation
OCH3
COOH
Carboxylic acid C8H8O3
HI
—CH3I
OH
COOH
p-hydroxy-benzoic acid

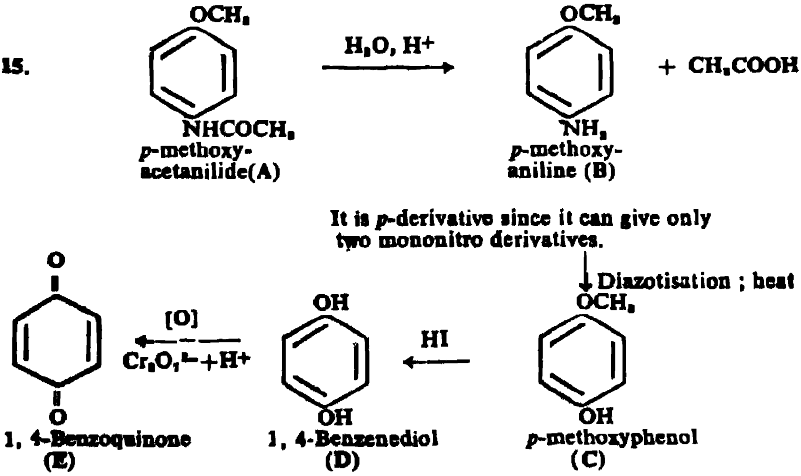
13. B is $C_7H_6NBr_3$; A is *m*- toluidine



14.

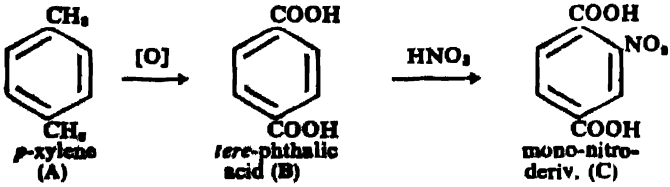


15.

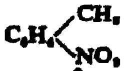


It is *p*-derivative since it can give only two mononitro derivatives.

16.



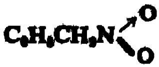
17.



$C_6H_4\langle^{CH_3}_{NO_2}$

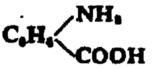
o-, *m*- & *p*-
Nitrotoluenes

$C_6H_5CH_2—O—N=O$
Benzyl nitrite



$C_6H_5CH_2N\langle^{O}_{O}$

Phenylnitro-
methane

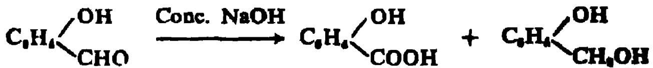


$C_6H_4\langle^{NH_2}_{COOH}$

o-, *m*- & *p*
Aminobenzoic acid

18. $C_6H_5CHBr.CH_2Br \longleftarrow C_6H_5CH{=}CH_2 \xrightarrow{[O]} C_6H_5COOH$

(C) containing 60·6% bromine; Styrene (A); Benzoic acid (B)

19. 

o-, m- & p-hydroxybenzaldehyde (A) — Conc. NaOH → o-, m- & p-hydroxybenzoic acid (B) + o-, m- & p-hydroxybenzyl alcohol (M)

(B) can be obtained by oxidation of (A)

↓ Soda-lime

C_6H_5OH
Phenol

(M) can be obtained by reduction of (A)

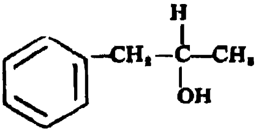
20. $C_6H_5CH{=}O \xrightarrow{NH_2OH} C_6H_5CH{=}NOH$

Benzaldehyde (A); Oxime

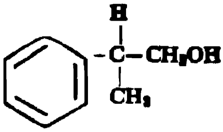
Acetic anhydride + Sod acetate ↓

$C_6H_5CH{=}CH\ COOH$
cinnamic acid
(B)

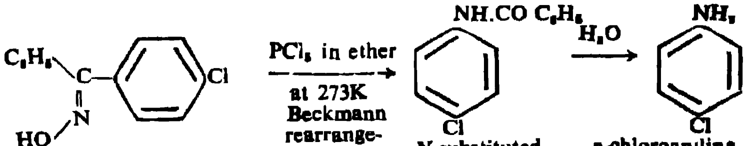
B decolorises alkaline $KMnO_4$ (property of C=C) and liberates CO_2 from $NaHCO_3$ with effervescence (property of COOH group)

21. 

1-Phenyl-2-propanol
A

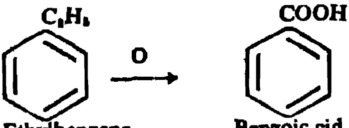


2-Phenyl-1-propanol
B

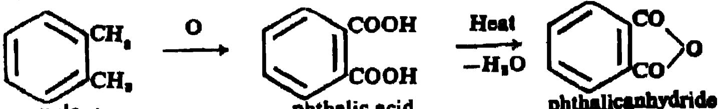
22. 

Ketoxime → N-substituted amide → p-chloroaniline + C_6H_5COOH Benzoic acid

In Beckmann rearrangement Cl—C_6H_4— being anti-R group migrates from carbon to nitrogen. It is the conversion of a ketoxime to N-substituted amide.

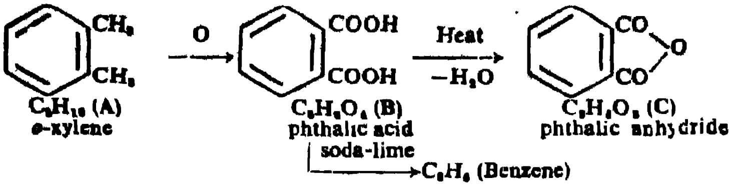
23. 

Ethylbenzene (A) → Benzoic cid



o-xylene (B) → phthalic acid → phthalicanhydride (C)

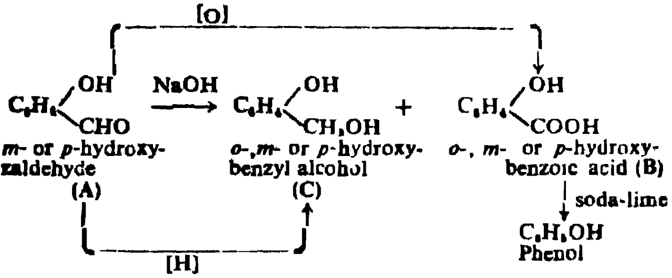
24.



C_8H_{10} (A) *o*-xylene $\xrightarrow{O}$ $C_8H_6O_4$ (B) phthalic acid $\xrightarrow[-H_2O]{\text{Heat}}$ $C_8H_4O_3$ (C) phthalic anhydride

phthalic acid $\xrightarrow{\text{soda-lime}}$ C_6H_6 (Benzene)

25.



$C_6H_4\langle^{OH}_{CHO}$ $\xrightarrow{NaOH}$ $C_6H_4\langle^{OH}_{CH_2OH}$ + $C_6H_4\langle^{OH}_{COOH}$

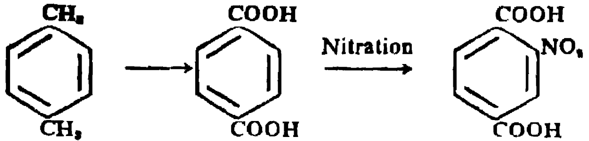
o-, *m*- or *p*-hydroxy-benzaldehyde (A)

o-,*m*- or *p*-hydroxy-benzyl alcohol (C)

o-, *m*- or *p*-hydroxy-benzoic acid (B)

$\xrightarrow{\text{soda-lime}}$ C_6H_5OH Phenol

26.

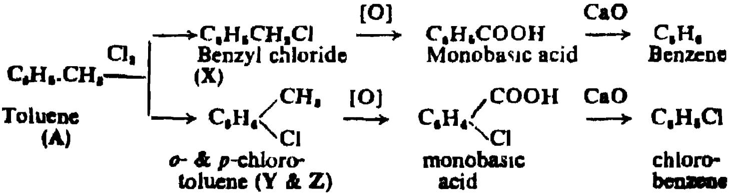


p-xylene (A)

tere-phthalic acid (B)

only one mono-nitro compound

27.



$C_6H_5.CH_3$ Toluene (A) $\xrightarrow{Cl_2}$ $C_6H_5CH_2Cl$ Benzyl chloride (X) $\xrightarrow{[O]}$ C_6H_5COOH Monobasic acid $\xrightarrow{CaO}$ C_6H_6 Benzene

$\xrightarrow{Cl_2}$ $C_6H_4\langle^{CH_3}_{Cl}$ *o*- & *p*-chloro-toluene (Y & Z) $\xrightarrow{[O]}$ $C_6H_4\langle^{COOH}_{Cl}$ monobasic acid $\xrightarrow{CaO}$ C_6H_5Cl chloro-benzene

28. $C_6H_5\,CONH_2$ $\xrightarrow{NaBrO}$ $C_6H_5\,NH_2$ $\xrightarrow{Ac_2O}$ $C_6H_5\,NH.COCH_3$

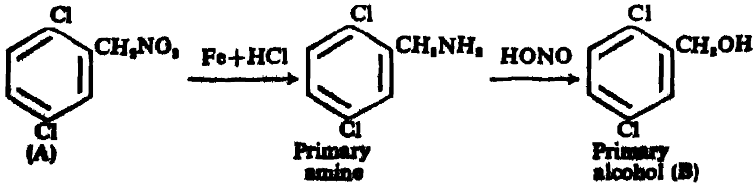
Benzamide (A) — Hofmann degradation — Aniline (B) — Acetanilide (C)

29. $C_{10}H_{16}O$ $\xrightarrow{HNO_3}$ $C_{10}H_{16}C_4$

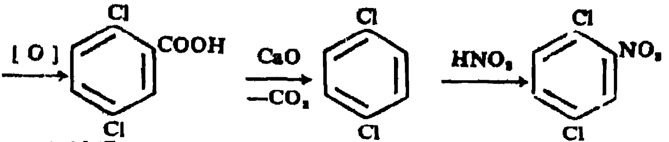
Camphor (A) — Camphoric acid (B)

(*A dibasic acid* shown by its Mol. wt.=200 and Eq. wt. given=100)

30.



(A) Primary amine Primary alcohol (B)

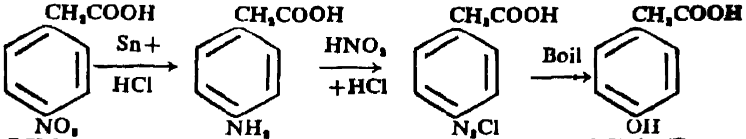


Acid (Eq wt=191) (C)

p-dichloro-benzene (D)

only one nitro deriv.

31.

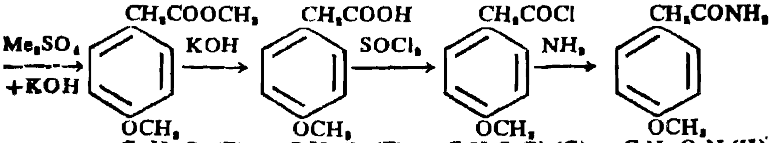


$C_8H_7NO_4$ (A) *p*-nitrophenylacetic acid

$C_8H_9NO_2$ (B) *p*-aminophenylacetic acid

$C_8H_7N_2O_2Cl$ (C) *p*-diazophenylacetic acid

$C_8H_8O_3$ (D) *p*-hydroxyphenylacetic acid

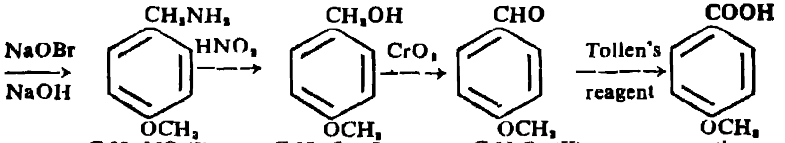


$C_{10}H_{12}O_3$ (E) methyl ester of *p*-methoxy-phenylacetic acid

$C_9H_{10}O_3$ (F) *p*-methoxyphenylacetic acid

$C_9H_9O_2Cl$ (G) *p*-methoxyphenylacetyl chloride

$C_9H_{11}O_2N$ (H) *p*-methoxyphenylacetamide



$C_8H_{11}NO$ (I) *p*-methoxybenzylamine

$C_8H_{10}O_2$ (J) *p*-methoxybenzyl alcohol

$C_8H_8O_2$ (K) *p*-methoxybenzaldehyde

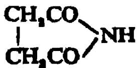
p-methoxybenzoic acid

32. A is $(CH_3)_2C{=}CH.CH_2.CH_2.CO.CH_3$ $(C_8H_{14}O)$
6-Methyl-5-hepten-2-one

B is $CH_3.CO.CH_2.CH_2.CHO$ $(C_5H_8O_2)$
4-Oxopentan-1-al

C is $HOOC{-}CH_2{-}CH_2{-}COOH$ $(C_4H_6O_4)$
Succinic acid

D is



$$\begin{matrix} CH_2CO \\ | \\ CH_2CO \end{matrix}\!\!>NH$$

$(C_4H_5O_2N)$

Succinimide

33. $$2\,C_6H_5CHO \xrightarrow{NaOH} C_6H_5CH_2OH + C_6H_5COONa$$

Benzaldehyde (A) Benzyl alcohol (B) Sod. salt of Benzoic acid (C)

$$C_6H_5CH_2OH \xrightarrow{O} C_6H_5COOH \xrightarrow[\text{lime}]{\text{Soda}} C_6H_6$$

(B) (C) Benzene

34. A is $CH_3.CO.CH(CH_3)_2$ $(C_5H_{10}O)$
3-Methyl-2-butanone

B is $CH_3.CHOH.CH(CH_3)_2$ $(C_5H_{12}O)$
3-Methyl-2-butanol

C is $CH_3CH{=}C(CH_3)_2$ (C_5H_{10})
2-Mthyl-2-butene

D is CH_3CHO (Ethanal) (C_2H_4O)

and E is $CH_3.CO.CH_3$ (Propanone) (C_3H_6O)

35. Empirical formulae A, B and M are C_7H_7Cl, $C_7H_6O_2$ and C_7H_8O respectively.

A on oxidation loses Cl atom, it must be present in the side chain which as a whole is oxidised to COOH group,

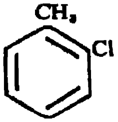
A is $C_6H_5CH_2Cl$ (Benzyl chloride)

B is C_6H_5COOH (Benzoic acid)

M is $C_6H_5CH_2OH$ (Benzyl alcohol)

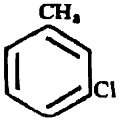
$$\underset{\substack{\text{Benzyl alcohol}\\ \text{M } (EF\ C_7H_8O)}}{C_6H_5CH_2OH} \xleftarrow{NaOH} \underset{\substack{\text{Benzyl chloride}\\ \text{A } (EF\ C_7H_7Cl)}}{C_6H_5CH_2Cl} \xrightarrow{KMnO_4} \underset{\substack{\text{Benzoic acid}\\ \text{B } (FEC_7H_6O_2)}}{C_6H_5COOH}$$

Isomers of A



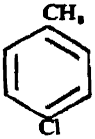
o-Chlorotoluene

;



m-chlorotoluene

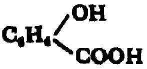
;



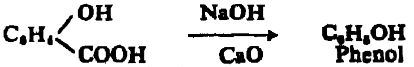
p-chlorotoluene

They give different products on oxidation and hydrolysis.

36. Molecular formula of the monobasic acid is $C_7H_6O_3$. The acid gives a product with soda-lime that should be phenol (violet colour with $FeCl_3$).

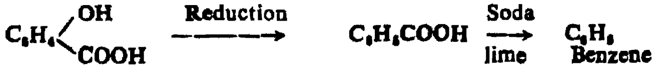
So it could be a phenolic acid, 

$C_6H_4\langle^{OH}_{COOH}$



$$C_6H_4\langle^{OH}_{COOH} \xrightarrow[CaO]{NaOH} \underset{\text{Phenol}}{C_6H_5OH}$$

o-, *m*- or *p*-hydrodxy-
benzoic acid



$$C_6H_4\langle^{OH}_{COOH} \xrightarrow{\text{Reduction}} C_6H_5COOH \xrightarrow[\text{lime}]{\text{Soda}} \underset{\text{Benzene}}{C_6H_6}$$

37. (*i*) Empirical formula of (A) $-C_{14}H_{10}$

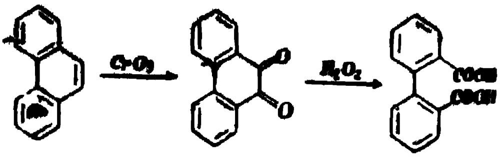
Empirical formula of $B{=}C_7H_4O$ and that of $C{=}C_7H_5O_2$;

$C_{14}H_{10}$ corresponds to anthracene.

(*ii*) Oxidation of anthracene gives anthraquinone while that of phenanthrene gives phenanthraquinone, both have the molecular formula, $C_{14}H_8O_2$. This is twice the empirical formula of (B).

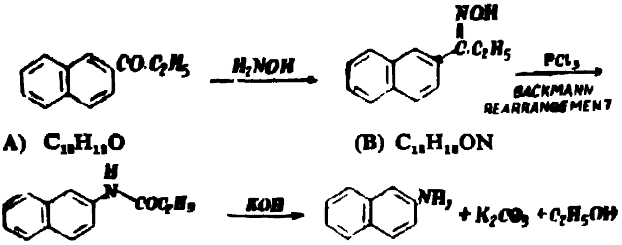
(*iii*) Oxidation of phenanthraquinone yields diphenic acid, $C_{14}H_{10}O_4$ (this is twice the empirical formula of C) while oxidation of anthraquinone yields alizarin, $C_{14}H_7O_4$ (this is not simply related to the empirical formula of C).

Hence (C) is diphenic acid, (B) is phenanthraquinone and (A) is phenathrene.



(A) $C_{14}H_{10}$ (B) $C_{14}H_8O_2$ (C) $C_{14}H_{10}O_4$

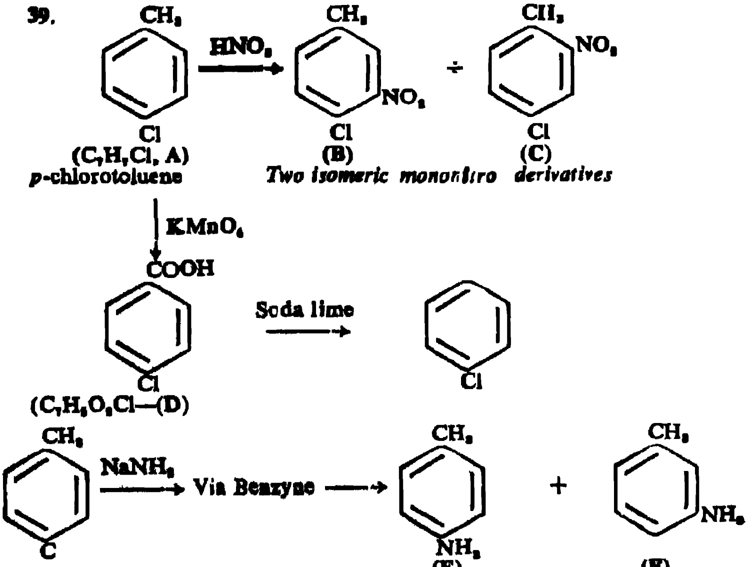
38. **Hints.** The final compound is 2-naphthylamine, so (A) is a naphthalene derivative. The reaction of (A) with NH_2OH indicates the presence of $>C{=}O$ group. The formula $C_{13}H_{12}O$ indicates the presence of an alkyl group, C_2H_5 (naphthyl is $C_{10}H_7-$). The reactions are :



(A) $C_{13}H_{12}O$ (B) $C_{13}H_{13}ON$

(C) (Isomer of B) 2-naphthylamine

39.

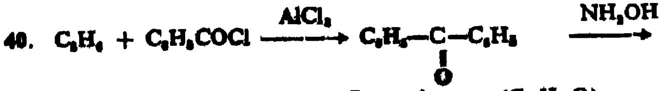


(C_7H_7Cl, A) p-chlorotoluene (B) (C) *Two isomeric mononitro derivatives*

($C_7H_5O_2Cl$—(D)

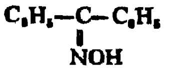
(E) (F) Both can be diazotised and coupled with 2-naphthol

40.



$$C_6H_6 + C_6H_5COCl \xrightarrow{AlCl_3} C_6H_5-\underset{\underset{O}{\|}}{C}-C_6H_5 \xrightarrow{NH_2OH}$$

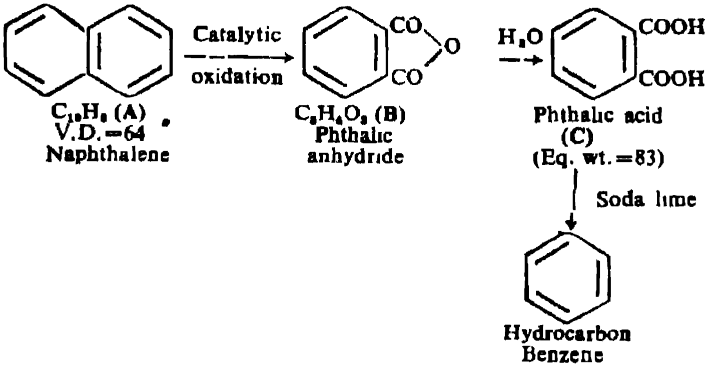
Benzophenone ($C_{13}H_{10}O$)
(A)



$$\underset{\substack{\text{Oxime } (C_{13}H_{11}ON)\\(B)}}{C_6H_5-\underset{\substack{\|\\NOH}}{C}-C_6H_5} \xrightarrow[\substack{\text{Beckmann}\\\text{rearrangement}}]{H_2SO_4,\ \text{Heat}} \underset{\substack{\textit{Benzanilide}\\(C)}}{C_6H_5CONHC_6H_5} \xrightarrow[NaOH]{}$$

$$\underset{\substack{\text{Liquid D } (C_6H_7N)\\\text{Aniline}}}{C_6H_5NH_2} \xrightarrow[\text{chilled}]{NaNO_2/\text{acid}} C_6H_5\overset{+}{N_2}\overset{-}{Cl} \xrightarrow[\text{coupling}]{\text{2-naphthol}} \text{Red dye}$$

41.



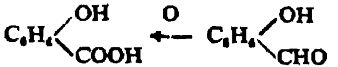
42. $$\underset{\substack{\text{Benzyl alcohol}\\(A)}}{C_6H_5CH_2OH} \xrightarrow{O} \underset{C_7H_6O\ (B)}{C_6H_5CHO} \xrightarrow{O} \underset{C_7H_6O_2\ (C)}{C_6H_5COOH}$$

$$\xrightarrow[\text{solution}]{NaOH} \underset{\substack{C_7H_5O_2Na\\(D)}}{C_6H_5COONa} \xrightarrow{\text{Soda lime}} \underset{\text{Benzene}}{C_6H_6}$$

43. $$\underset{\substack{C_{13}H_{10}O_2,\ (A)\\\text{Phenyl benzoate}}}{C_6H_5O.COC_6H_5} \xrightarrow[\text{boil}]{\text{alkali}} \underset{\substack{C_6H_6O,\ (C)\\\text{Phenol}}}{C_6H_5OH} + \underset{\substack{C_7H_6O_2,\ (B)\\\text{Benzoic acid}}}{C_6H_5COOH}$$

Phenol $\xrightarrow{CHCl_3,\ NaOH}$ Salicyaldehyde

Benzoic acid $\xrightarrow{C_2H_5OH,\ ZnCl_2}$ $C_6H_5COOC_2H_5$ ($C_9H_{10}O_2$, (D)) Ethyl benzoate



$$\underset{\substack{\text{Salicylic acid}\\(C_7H_6O_3,\ F)}}{C_6H_4\begin{matrix}OH\\COOH\end{matrix}} \xleftarrow{O} \underset{\substack{\text{Salicyaldehyde}\\(C_7H_6O_2,\ E)}}{C_6H_4\begin{matrix}OH\\CHO\end{matrix}}$$

$$\underset{\substack{C_6H_5COOC_2H_5\\(C_9H_{10}O_2,\ (D))\\\text{Ethyl benzoate}}}{}$$

44. $$\underset{\text{Benzonitrile (A)}}{C_6H_5C\equiv N} \xrightarrow[-NH_3]{KOH} \underset{\text{Benzoic acid (B)}}{C_6H_5COOH}$$

$[H]\ \big\downarrow$ Na, alcohol

$$\underset{\substack{\text{Benzylamine}\\(C)}}{C_6H_5CH_2NH_2} \xrightarrow[-N_2]{HNO_2} \underset{\substack{\text{Benzyl alcohol}\\(D)}}{C_6H_5CH_2OH} \xrightarrow{[O]} \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

Appendix III

MISCELLANEOUS QUESTIONS

(A) WHAT HAPPENS

1. What products are formed in the following reactions :

(*a*) Aniline is treated with dilute hydrochloric acid and sodium nitrite solution at 0° C.

(*b*) Salicylic acid is heated with acetic anhydride and sodium acetate.

(*c*) Succinic acid is heated.

(*d*) Concentrated sulphuric acid is added to glucose.

(*e*) Toluene is heated with potassium permanganate solution.

(*Andhra B.Sc. 1974*)

2. Give the structure of product or products in the following reactions:

(*a*) Pyrrole $\xrightarrow{CHCl_3,\ KOH}$

(*b*) Thiophene $\xrightarrow{CH_2O,\ HCl}$

(*c*) Furan + maleic anhydride$\rightarrow$

(*d*) Quinoline $\xrightarrow{KMnO_4}$

(*e*) Isoquinoline $\xrightarrow{KMnO_4}$ (*Andhra B.Sc. 1974*)

3. Predict the products in the following reactions :

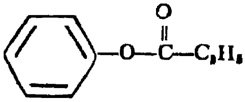
(*a*) Benzene $\xrightarrow{AlCl_3,\ \text{Succinic anhydride}}$

(*b*) *p*-Cresol $\xrightarrow{CHCl_3,\ NaOH}$

(*c*) Phthalimide $\xrightarrow{Br_2 + NaOH}$

(*d*) Ph—CH=CH—COPh $\xrightarrow{\text{Ethyl malonate} \quad NaOEt}$

(*e*)

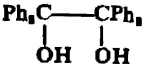


$\xrightarrow{AlCl_3}$ (*Calicut B.Sc. 1973*)

4. Predict the products in the following reactions :

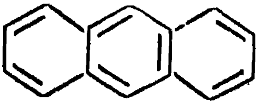
(*a*) Pyridine $\xrightarrow{NaNH_2,\ \text{Heat}}$

(*b*)



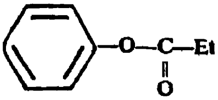
$Ph_2\underset{OH}{C}—\underset{OH}{C}Ph_2 \xrightarrow{H_2SO_4}$

(*c*)



$\xrightarrow{Na_2Cr_2O_7,\ H^+}$

(*d*)



$\xrightarrow{AlCl_3}$

(*e*) $C_6H_5NH.NHC_6H_5 \xrightarrow{H^+}$

5. What are the products obtained when

(*a*) Acetanilide is treated with bromine,

(*b*) Iodobenzene is reacted with chlorine and alkali added to the product,

(*c*) Methylaniline is acted upon by nitrous acid,

(*d*) Benzyl alcohol is reacted with concentrated hydrochloric acid,

(*e*) Benzophenone is fused with caustic potash ? (*Kerala B.Sc. 1973*)

6. What happens when

(*a*) Toluene is treated with chlorine,

(*b*) Benzenesulphonyl chloride is treated with ethylamine and alkali is added to the product,

(*c*) Nitrobenzene is reduced in alkaline medium,

(*d*) Aniline is treated with carbon disulphide and solid potash,

(*e*) Phenol is refluxed with carbon tetrachloride and alkali,

(*f*) Benzoic acid is distilled with acetic anhydride,

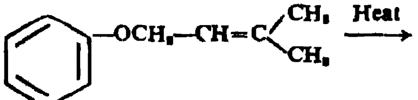
(*g*) Salicylic acid is treated with phosphorus pentachloride,

(*h*) Cinnamic acid is treated with chromic acid,

(*i*) Phthalic acid is heated with ammonia ? (*Kerala B Sc. 1972*)

7. What are the products obtained in the following reactions :

(*a*)



(*b*) $CH_2=CH-CH=CH_2 + CH_2=CH.CHO \longrightarrow$

(*c*) $C_6H_5CHO + HCHO \xrightarrow{OH^-}$ (*Madras B.Sc. 1974*)

8. What happens when

(*i*) Toluene is oxidised with alkaline potassium permanganate,

(*ii*) Acetophenone is reduced with sodium amalgam and alcohol,

(*iii*) Benzaldehyde is heated with alcoholic solution of potassium cyanide.

(*iv*) Diphenylamine reacts with nitrous acid ? (*Ravi Shankar B.Sc. 1972*)

9. State what happens when,

(*a*) Citric acid is treated with fuming H_2SO_4 at low temperature,

(*b*) Tartaric acid is treated with ice-cold H_2O_2 in presence of a trace of Fe^{2+} salt,

(*c*) Malonic ester is treated with HNO_3 in cold,

(*d*) *p*-Nitroaniline is boiled with alkali,

(*e*) Picric acid is treated with PCl_5 and the product so formed is boiled with water ? (*Burdwan B.Sc. 1974*)

10. What happens when

(*a*) Malonic acid is heated to 410-420K,

(*b*) Sodium nitrite and a few drops of HCl are added to an aqueous solution of urea,

(*c*) A solution of phenylhydrazine is added to an aqueous solution of glucose,

(*d*) Dry sodium phenate is heated with carbon dioxide in a closed vessel under pressure to 390-400K,

(*e*) Glycerol is heated with potassium bisulphate ? (*Burdwan B.Sc. 1970*)

11. Explain what happens when

(*a*) Urea is treated with oxalic acid in the presence of phosphoryl chloride, (*b*) Acetylene is passed into warm acetic acid in the presence of mercuric ions,

(*c*) Benzaldehyde is heated with a solution of formaldehyde in an alcoholic alkali,

(*d*) Thiourea is heated with ethyl alcohol and 48% hydrobromic acid,

(*e*) A mixture of 1, 3-benzenediol and phthalic anhydride is heated with a few drops of concentrated sulphuric acid and the reaction product is poured into dilute alkali ? (*Calcutta B.Sc. 1973*)

(B) TYPICAL CONVERSIONS

1. Outline how the following conversions may be effected :

(*a*) Aniline into acetanilide, (*b*) Benzene into toluene,
(*c*) Aniline into iodobenzene, (*d*) Formaldehyde into methyl alcohol,
(*e*) Acetic acid into acetamide. (*Andhra B.Sc. 1974*)

2. How may the following conversions be effected :

(*a*) Glucose into fructose, (*b*) Fructose into glucose,
(*c*) Aniline into quinoline, (*d*) Anthracene into alizarin,
(*e*) Sulphanilic acid to methyl orange ? (*Andhra B.Sc. 1974*)

3. How are the following interconversions carried out :

(*a*) D-glucose to D-fructose, (*b*) D-arabinose to D-glucose,
(*c*) D-glucose to D-mannose, (*d*) D-glucose to D-arabinose ?
(*Calicut B.Sc. 1974 ; Kerala 1975*)

4. How are the following conversions effected :

(*a*) Benzene to acetophenone, (*b*) Oxalic acid to formic acid,
(*c*) Phenol to salol, (*d*) Benzaldehyde to benzilic acid ?
(*Bangalore B.Sc. 1974 ; Kerala 1970*)

5. How do you convert :

(*i*) Methyl chloride into ethane, (*ii*) Toluene into benzyl chloride,
(*iii*) Anthracene into anthraquinone,
(*iv*) Phenol to salicylic acid, (*v*) Benzene to iodobenzene ?
(*Bangalore B.Sc. 1974, 72*)

6. Indicate how the following conversions may be brought about :

(*i*) Benzene to T.N.T , (*ii*) Toluene to benzaldehyde,
(*iii*) Phenol to aspirin, (*iv*) Acetic acid to acetoacetic ester,
(*v*) Naphthalene to phenolphthalein,
(*vi*) Benzaldehyde to cinnamic acid. (*Bangalore B.Sc. 1973*)

7. How are the following conversions carried out :

(*i*) Phenol into phenacetin, (*ii*) Naphthalene into 2-napthylamine,
(*iii*) Glucose into fructose. (*Bombay B.Sc. 1975*)

8. How will you carry out the following conversions :

(*a*) Glucose into fructose, (*b*) Naphthalene into naphthylamine,
(*c*) Anthracene into alizarin, (*d*) Benzene into T.N.T.,
(*e*) Benzene into 1, 3-benzenediol. (*Bombay B.Sc. 1972, 71*)

9. How would you convert :

(*a*) Glucose into fructose ; (*b*) Phenol into benzene ;
(*c*) Fructose into glucose ? (*Delhi B.Sc. 1972*)

10. How will you obtain :

(*a*) Toluene from benzene, (*b*) *m*-nitrotoluene from toluene,
(*c*) *m*-diaminobenzene from benzaldehyde. (*Delhi B.Sc. 1972*)

11. How would you convert any four of the following :

(a) An aldose into a ketose ; (b) A pentose into a hexose ;

(c) Benzene into salicylaldehyde ; (d) Benzene into 1, 3-benzenediol ;

(e) Benzene into *o*-nitroaniline ? *(Delhi B.Sc. 1971)*

(C) HOW WILL YOU PREPARE

1. How will you obtain :

(a) Meta-nitraniline from meta-dinitrobenzene,

(b) Azobenzene from nitrobenzene, (c) Meta-nitrotoluene from toluene,

(d) Cinnamic acid from benzaldehyde ? *(Jabalpur B.Sc. 1973)*

2. How would you obtain the following :

(a) Phenol from Benzene. (b) Cinnamic acid from malonic ester.

(c) Salicylic acid from phenol ? *(Madras B.Sc. 1971)*

3. How will you obtain the following :

(1) Anthranilic acid from phthalic acid.

(2) *m*-nitrotoluene from benzene. (3) Succinic acid from ethanol.

(4) Oxalic acid from sucrose. (5) *m*-nitroaniline from Benzene.

(Nagpur B.Sc. 1973)

4. Outline the steps for the preparation of following :

(1) Ethyl acetoacetate from acetic acid.

(2) Acetophenone from benzyl alcohol. (3) 2-naphthol from naphthalene.

(4) Iodobenzene from diazonium chloride.

(5) Benzoic acid from cinnamic acid. *(Madras B.Sc. 1973)*

5. Starting from benzene, show how you would prepare :

(i) Iodobenzene. (ii) Aspirin.

(iii) T.N.T. *(Bombay B.Sc. 1975)*

6. How do you obtain the following :

(i) Allyl alcohol from glycerol. (ii) *s*-trinitrobenzene from T.N.T.

(iii) Cinnamic acid from benzaldehyde, and ethyl acetate ?

(Burdwan B.Sc. 1974)

7. How will you prepare :

(a) *p*-Hydroxyazobenzene from aniline ;

(b) Fluorescein from phthalic acid ; (c) Aniline from sulphanilic acid ;

(d) Meta-nitroaniline from benzene ? *(Delhi B.Sc. 1972)*

8. How will you obtain—

(a) Benzylamine from Benzaldehyde,

(b) Hydroxylamine from Nitrobenzene,

(c) Cinnamic acid from Benzyl chloride,

(d) Phenylhydrazine from Aniline, (e) Picric acid from Salicylic acid,

(f) Phenol from Salicylaldehyde, and (g) Benzophenone from Benzene ?

(Rajasthan B.Sc. 1971)

(D) HOW WILL YOU DISTINGUISH BETWEEN

1. How are the following pairs of compounds distinguished by means of their reactions :

(a) Decalin from naphthalene,

(b) Cyclopropane from ethylene,

(c) Vinyl chloride from allyl chloride,

(d) Acetylene from ethylene ? *(Madras B.Sc. 1973)*

2. How are the following distinguished by their reactions :

(*a*) Benzoquinone from benzophenone,

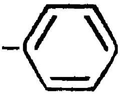
(*b*) Salicylaldehyde from acetophenone,

(*c*) Diacetyl from acetic anhydride,

(*d*) Acetyl chloride from ethyl chloride,

(*e*) Glucose from fructose. (*Madras B.Sc. 1973*)

3. How would you distinguish between :

(*i*) HO—CH_2—

and HO

(*ii*) $CH_3COCH_2CH_2CH_3$ and $CH_3CH_2COCH_2CH_3$

(*iii*) $CH_3CH{=}CH{-}CH{=}CHCH_3$ and $CH_3CH{=}CH{-}CH_2{-}CH{=}CH_2$? (*Madras B.Sc. 1971*)

4. How would you distinguish between :

(*a*) 2, 4-dimethylaniline and *N*, *N*-dimethylaniline.

(*b*) Benzamide and acetanilide.

(*c*) *n*-pentane and 1-methyl-2-ethylethylene.

(*d*) 2-naphthol and 2-naphthyl methyl ether.

(*e*) Benzaldehyde and diphenyl ketone.

(*f*) 3, 5-dichlorobenzoic acid and methyl 3, 5-dichlorobenzoate ? (*Osmania B.Sc. 1971*)

5. Give one chemical test in each case to distinguish :

(*i*) formaldehyde from acetaldehyde. (*ii*) acetaldehyde from acetone.
(*iii*) Benzoic acid from salicylic acid. (*Bangalore B.Sc. 1974*)

(E) STRUCTURAL FORMULAE

1. Write down the structural formulae of :

(*a*) methyl orange, (*b*) 1,2,3-benzenetriol (*c*) 3-methylbenzenol
(*d*) isoquinoline, (*e*) phthalic anhydride, (*f*) 2-nitronaphthalene
(*g*) azobenzene, and (*h*) *o*-xylene.

2. Give the structural formulae of :

(*i*) DDT, (*ii*) Picric acid, (*iii*) Saccharin,
(*iv*) Gammexane, (*v*) Glucose, (*vi*) Benzenesulphonic acid,
(*vii*) Chloramine-T, (*viii*) Benzoin.

3. Give the structural formulae of :

(1) Chloramine T, (2) Saccharin, (3) Aspirin,
(4) Triphenylmethane, (5) Cinnamic acid, (6) Azoxybenzene,
(7) TNT, (8) Meta-toluidine, (9) *p*-aminoazobenzene,
(10) Hippuric acid.

4. Give the structural formulae of the following substances :

(*a*) *p*-Bromotoluene and benzyl bromide ;

(*b*) Benzamide and acetanilide ; (*c*) Phenol and salicylic acid ;

(*d*) Methyl ether of salicylic acid and methyl salicylate ;

(*e*) *N*-Methylaniline and toluidine ;

(*f*) Bezyl alcohol and methylbenzenol

5. Write structural formulae of the following compounds :

(*a*) Acetophenone-oxime, (*b*) Benzanilide, (*c*) DDT,
(*d*) Saccharin, (*e*) Phenolphthalein, (*f*) T.N.T.
(*g*) *p*-Quinone, and (*h*) Pyrog

(F) NAME REACTIONS

Write short notes on :

1. Friedel-Crafts reaction. (*Calicut B.Sc. 1973 ; Nagpur 1973 ; Ravishankar 1972 ; Bhagalpur 1972 ; Punjab and Guru Nanak T.D.C. 1971*)
2. Fittig's reaction.
3. Kolbe's synthesis. (*Delhi B.Sc. 1972 ; Punjab 1971*)
4. Perkin's reaction. (*Punjab & Guru Nanak B.Sc. 1971 ; Delhi 1972*)
5. Sandmeyer's reaction. (*Ravishankar B.Sc. 1972*
6. Reimer-Tiemann reaction. (*Punjab B.Sc. 1971 ; Delhi 1971*)
7. Claisen's condensation. (*Delhi B.Sc 1971 ; Punjab 1971*)
8. Gattermann's reaction.
9. Rosenmund's reaction.
10. Clemmensen reduction. (*Calicut B.Sc. 1973*)
11. Schotten-Baumann reaction. (*Bhagalpur B.Sc. 1972*)
12. Hofmann degradation. (*Punjab B.Sc. 1971*)
13. Cannizzaro reaction. (*Punjab B.Sc. 1971 ; Delhi 1972*)
14. Gabriel phthalimide reaction.
15. Grignard reaction.
16. Wurtz-Fittig reaction.
17. (*i*) Dieckmann cyclisation. (*ii*) Diels-Alder reaction.
    (*iii*) Beckmann transformation.
18. (*i*) Benzidine transformation.
    (*ii*) Ullmann reaction. (*Kerala B.Sc. 1973*)
19. Skraup synthesis. (*Delhi B.Sc. 1972, 71*)
20. (*i*) Schmidt reaction ; (*ii*) Hofmann rearrangement ;
    (*iii*) Fischer-Hepp rearrangement ;
    (*iv*) Bart's reaction ; (*v*) Benzidine transformation.
21. (*a*) Hofmann Rearrangement.
    (*b*) Houben-Hoesch synthesis.
    (*c*) Benzoin Condensation. (*Calicut Univ. 1973*)
22. (*a*) Claisen Rearrangement.
    (*b*) Skraup synthesis. (*Calicut B.Sc. 1972*)
23. Houben-Hoesch reaction. (*Kerala B.Sc. 1973*)
24. (*a*) Reformatsky reaction, (*b*) Etard reaction. (*Kerala B.Sc. 1972*)
25. (*a*) Claisen synthesis ; (*b*) Benzoin Condensation. (*Nagpur B.Sc. 1973*)
26. Fries rearrangement.
27. Arndt-Eistert synthesis.

(G) IMPORTANT REAGENTS

1. Discuss the use of the following in Organic Chemistry :

(*a*) Phenylhydrazine ; (*b*) Anhydrous aluminium chloride ;
(*c*) Schiff's reagent ; (*d*) Tollen's reagent ;
(*e*) 2-Naphthol ; (*f*) Zinc dust ;
(*g*) Ferric chloride ; and (*h*) Copper sulphate.

2. Discuss the uses of the following reagents :

(*a*) Nitrous acid.
(*b*) (*i*) Aluminium chloride.
(*ii*) Acetyl chloride. (*iii*) Zinc dust.
(*iv*) Alcoholic potassium hydroxide.
(*v*) Carbon tetrachloride.

(*e*) (*i*) Potassium cyanide. (*ii*) Sodium hydroxide.

(*iii*) Bromine. (*iv*) HNO_3.

(*v*) Lithium aluminium hydride.

(*vi*) Aluminium isopropoxide.

(H) SHORT NOTES

1. Write short notes on any three of the following :

(*a*) Crum-Brown-Gibson's Rule. (*b*) Dehydrogenation.

(*c*) Purification of benzene. (*d*) Decalin.

2. Write short notes on any three of following based on electronic conception :

(*i*) Fridel-Crafts Ketone synthesis. (*ii*) Aldol condensation.

(*iii*) Addition of HBr to propylene in the presence of peroxide.

(*iv*) Lewis acids.

3. Write short notes on any two of the following :

(*a*) Separation of primary, secondary and tertiary amines.

(*b*) Orientation in benzene ring.

(*c*) Racemic and meso-tartaric acids.

4. Write notes on any three of the following :

(*a*) Crum-Brown and Gibson Rule. (*b*) Phthalein dyes.

(*c*) Cannizzaro reaction. (*d*) Coupling reaction.

(*e*) Perkin reaction.

5. Explain and illustrate any three of the following :

(*i*) Formylation, (*ii*) Chlorination of toluene,

(*iii*) Resemblance between the reactions of phenol and pyrrole,

(*iv*) Friedel-Crafts reaction, and (*v*) Reimer-Tiemann reaction,

6. Write notes on the following examples :

(*i*) Directive influence of groups in aromatic substitution,

(*ii*) Friedel-Crafts reaction,

(*iii*) Reimer-Tiemann reaction, and

(*iv*) Sandmeyer reaction.

(I) HOW WILL YOU SHOW

1. Give evidence to show that—

(*a*) Benzene has a special structure which is saturated as well as unsaturated (modern concept) ;

(*b*) Naphthalene has two benzene rings ;

(*c*) Glucose has a pyranose ring ; and

(*d*) Quinone does not have aromatic character.

2. How will you show that :

(*a*) Phenol is acidic in nature ; and

(*b*) The unsaturated character of benzene is somewhat different from olefins ?

(J) ORGANIC ANALYSIS

1. Give the characteristic tests for the detection of the following groups when they are present in an organic compound :

(*a*) Acetyl ; (*b*) Aldehyde ;
(*c*) Ketonic ; (*d*) Carboxyl.

2. Give the characteristic tests for the detection of the following groups :

(*a*) Nitro ; (*b*) primary amine ; (*c*) amido ; (*d*) acetyl ;
(*e*) aldehydic ; (*f*) ketonic ; (*g*) phenolic hydroxyl ; (*h*) carboxyl ;

when they are present in aromatic compounds.

(K) HOW WILL YOU SEPARATE

1. You are given a mixture of benzene, aniline and phenol. How would you obtain from it a pure specimen of each and how would you identify each?

(L) EXPLAIN WHY

1. Sulphonation of naphthalene is a temperature controlled reaction. (*Delhi B.Sc. 1982*)

2. In anthracene the 9,10 positions are usually attacked. (*Delhi BSc. 1882*)

3. Electrophilic substitution of pyrrole is easier than in the case of ne. (*Delhi B.Sc. 1982*)

4. Electrophilic substitution of pyridine is difficult to achieve. (*Delhi B.Sc. 1982*)

Appendix IV

NEW TYPE QUESTION BANK—(III)

Short Answer Type :

1. What types of substances are included in the term carbohydrates now ?

2. Give molecular formulae of (*i*) arabinose, (*ii*) glucose, (*iii*) fructose, (*iv*) sucrose, (*v*) maltose, (*vi*) starch, (*vii*) cellulose.

3. Write equations for the hydrolysis of (*i*) sucrose, (*ii*) starch, (*iii*) inulin.

4. Write equations for the conversion of glucose into fructose and *vice-versa.*

5. Write down the configurational formulae for D-glucose and D-fructose and answer the following question :

Would they give the same or different osazone ? Explain with equations. (*Burdwan B.Sc., 1977*)

6. Name the monosaccharides which the following give on hydrolysis :

(*i*) sucrose, (*ii*) maltose, (*iii*) lactose,
(*iv*) starch, (*v*) inulin.

7. How is glucose obtained from cane sugar ?
(*Delhi B.Sc. Hons. Sub., 1977*)

8. Starting from glucose how can you obtain—
(*i*) Osazone, (*ii*) Sorbitol, (*iii*) Fructose, (*iv*) *n*-hexane ?
(*Delhi B.Sc. Hons. Sub., 1977*)

9. Why can't we substitute starch by cellulose (grass) in our food whereas grazing animals can ?

10. What are proteins ?

11. What are various functions of proteins ?

12. What are essential amino acids ?

13. What is peptide linkage ? What are dipeptides and tri-peptides ?

14. What are proteins used as catalysts called ?

15. What are products of hydrolysis of proteins ?

16. Name two textile fibres which are proteins.

17. Discuss the use of proteins in controlling body processes.

18. What is the difference between a polypeptide and a protein ?

19. What are conjugated proteins ? How are they classified ?
(*Delhi B.Sc. Hons., 1976*)

20. How may different polypeptides differ from one another ? What do you know about the spiral structure of proteins ?

21. What are the building blocks of proteins ? What are fibrous proteins ? Give two characteristics of these.

22. What are globular proteins ? Give two characteristics of these.

23. What is denaturation of protein ?

24. What are ureides ? How are they classified ?

25. Write names and formulae of products obtained in the following reactions :

(*i*) Acetamide+$COCl_2\rightarrow$ (*ii*) Oxalic acid+urea$\rightarrow$
(*iii*) Malonic ester+urea$\rightarrow$ (*iv*) Glycollic acid+urea$\rightarrow$
(*v*) Acetoacetic ester+urea$\rightarrow$

26. Write structures of—

(*i*) Pyrimidine ring ; (*ii*) Imidazole or iminazole ring ; (*iii*) Purine.

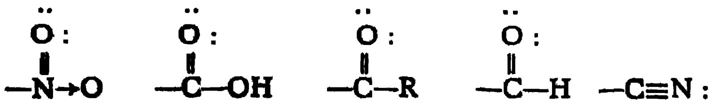
27. How are the following related to each other ?

(*i*) Uric acid ; (*ii*) Xanthine ; (*iii*) Caffeine.

(*Delhi B.Sc. Hons., 1976*)

28. Starting from cyanoacetic ester how would you synthesise uric acid ? (*Delhi B.Sc. Hons., 1976*)

29. Nitrobenzene stabilises itself by resonance. The following groups are of the same type :



$$-\overset{\overset{\ddot{O}:}{\|}}{N}\rightarrow O \qquad -\overset{\overset{\ddot{O}:}{\|}}{C}-OH \qquad -\overset{\overset{\ddot{O}:}{\|}}{C}-R \qquad -\overset{\overset{\ddot{O}:}{\|}}{C}-H \qquad -C\equiv N:$$

Write resonance structures showing stabilization by resonance of the benzene compounds containing each of the groups.

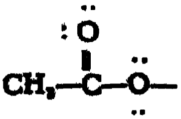
30. (*a*) Write one resonance structure for acetanilide which does not involve electrons of the ring. You will find it involves (+) and (—) charges.

(*b*) Explain on the basis of the resonance structure written by you, why acetanilide is less reactive towards electrophilic substitution than aniline.

31. Acetamide group (—$NHCOCH_3$) is an ortho-para director and acetanilide is much more reactive than benzene. Can you account for these facts on the basis of resonance structures which involve the benzene ring ?

32. Do you expect phenyl acetate to be more or less reactive than phenol ? Give reasons.

33. What is the directive influence of acetoxy group,



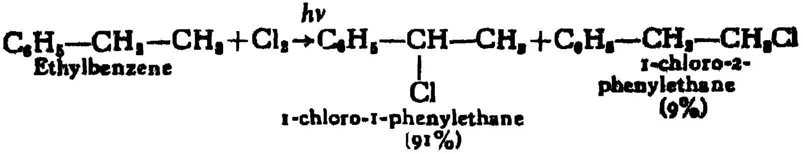
$$CH_3-\overset{\overset{:\ddot{O}}{\|}}{C}-\ddot{\underset{\cdot\cdot}{O}}-$$

in phenyl acetate ?

34. Compared to benzene, is phenyl acetate more or less reactive in electrophilic substitution ?

35. Why does side-chain halogenation of an alkyl-benzene occur preferentially at the benzylic hydrogen ? Explain at length ?

36. Chlorination of ethylbenzene in presence of sunlight is represented as follows :



$$\underset{\text{Ethylbenzene}}{C_6H_5{-}CH_2{-}CH_3} + Cl_2 \xrightarrow{h\nu} \underset{\substack{\text{1-chloro-1-phenylethane}\\(91\%)}}{C_6H_5{-}\underset{\substack{|\\ Cl}}{CH}{-}CH_3} + \underset{\substack{\text{1-chloro-2-}\\ \text{phenylethane}\\ (9\%)}}{C_6H_5{-}CH_2{-}CH_2Cl}$$

(a) How can you justify the formation of 1-chloro-1-phenylethane as a major product ?

(b) What kind of free radical is involved in the formation of 2-chloro-1-phenylethane (a minor product) ?

37. Name the major product you expect to be formed when n-propylbenzene is chlorinated in sunlight.

38. Write resonance structures of benzyl cation, $C_6H_5CH_2^+$.

39. Benzyl cation is more stable than a tertiary carbocation. Can you account for its exceptional stability ?

40. Would you expect that the positive charge of benzyl cation is delocalised ? If so, over which carbons ?

41. What does molecular orbital theory tell us about the location of the positive charge in benzyl cation ?

42. Write an explanatory note on inert character of chlorine in chlorobenzene. *(Delhi B.Sc., 1976)*

43. Give mechanism of chlorination of benzene. How is chlorobenzene obtained on a large scale ? *(Delhi B.Sc., 1976 Supp.)*

44. Explain why chlorobenzene is not acted upon by aqueous NaOH solution and alcoholic ammonia under ordinary conditions. *(Delhi B.Sc., 1976 Supp.)*

45. Account for the fact that 2, 4-Dinitrochlorobenzene is more reactive than chlorobenzene when treated with sodium hydroxide. *(Calicut B.Sc., 1973)*

46. Write equations for the following steps involved in the sulphonation of benzene :

(i) Production of SO_3 from H_2SO_4.

(ii) Formation of σ complex from $C_6H_6+SO_3$.

(iii) Abstraction of proton from the σ complex by the base (HSO_4^-) to give $C_6H_5SO_3^-$.

(iv) Reaction between $C_6H_5SO_3^-$ and H_3O^+.

47. Sulphonation is a reversible process. With conc. H_2SO_4 position of equilibrium lies appreciably to the right. With a high

concentration of water (on passing steam or with dilute H_2SO_4) equilibrium shifts to the left. It shifts further to left with volatile aromatic compound which distils over with steam.

Show all steps of desulphonation when benzenesulphonic acid is heated with dilute sulphuric acid.

48. In most desulphonation reactions the electrophile is a proton. Other electrophiles may, however, be used.

When benzenesulphonic acid reacts with bromine in presence of $FeBr_3$, bromobenzene is obtained. Name the electrophile in this reaction. Write various steps involved in the mechanism for this reaction.

49. On sulphonation of toluene at 273K and 373K the following proportions of monosubstituted products are obtained :

	ortho	*para*	*meta*
273K	43%	53%	4%
373K	13%	79%	8%

(*a*) Keeping in mind that sulphonation reactions are reversible, how can you account for the difference in the relative proportions of the three products at the lower and higher temperatures ?

(*b*) Which toluenesulphonic acid appears to be more stable, ortho or para ?

50. Give the mechanism of nitration of benzene with conc. HNO_3 and conc. H_2SO_4. (*Delhi B Sc. Hons., 1976, 77*)

51. On what factors does the number of nitro-groups introduced during nitration of a compound depend ?

52. What happens when aniline is

(*a*) warmed with $CHCl_3$ and KOH,

(*b*) treated with cold $NaNO_2$ solution and HCl,

(*c*) acetylated ? (*Delhi B Sc. Hons. Sub., 1976 Supp.*)

53. Why is aniline less basic than methylamine ? (*Nagpur B.Sc., 1973*)

54. Write mechanism for the ammonolysis of halogeno-compounds with liquid ammonia giving necessary conditions.

55. Para nitrosation of *N*, *N*-dimethylaniline $C_6H_5N(CH_3)_2$ is an example of C-nitrosation believed to be a nucleophilic substitution reaction in which NO^+ ion is the nucleophile.

(*a*) Explain how NO^+ ions are formed in an aqueous solution of $NaNO_2$ and HCl.

(*b*) Write the steps involved to explain the mechanism of the above C-nitrosation.

56. Tertiary aromatic amines and phenols undergo C-nitrosation reaction whereas most of the other aromatic compounds do not. Assign reasons for this difference in behaviour.

57. What is diazotisation ? Discuss its mechanism ?
(*Delhi B.Sc., Hons. 1977 ; Nagpur B.Sc. 1974 Supp.*)

58. How does a diazonium salt differ from a diazo-compound? (*Delhi B. Sc. Hons. 1977, 76*)

59. By using diazo reaction as one of the steps in the process, show how you would obtain the following from aniline :

(*a*) (*i*) 1,3, 5-tribromobenzene ; (*ii*) phenol ;
(*iii*) *p*-hydroxyazobenzene. (*Delhi B.Sc. Hons., 1976*)

(*b*) (*i*) Phenylhydrazine, (*ii*) Methoxybenzene,
(*iii*) Diazoaminobenzene. (*Nagpur B.Sc., 1974 Supp*)

60. Excess of mineral acid is used in diazotisation process. Suggest reasons.

61. Benzenediazonium chloride couples with phenol but not with methoxybenzene. Explain why ?

62. 2, 4-Dinitrobenzenediazonium chloride couples with methylbenzene (anisole) and 2, 4, 6-Trinitrobenzenediazonium chloride couples even with mesitylene. Give reasons.

63. Account for the following :

(*a*) Out of three isomeric nitrophenols only the *o*-isomer is steam volatile and its boiling point and solubility are lower as compared to the other isomers.

(*b*) Unlike most phenols, 2, 4-dinitrophenol and 2, 4, 6-trinitrophenol are soluble in aqueous sodium bicarbonate.

64. Formulate a reaction scheme to synthesise phenol from benzene and make use of Friedel-Crafts reaction.
(*Punjab B.Sc., 1975*)

65. Give the probable mechanism of Reimer-Tiemann Reaction. (*Punjab B.Sc., 1976 Supp.*)

66. Name the reagents and reaction conditions for the preparation of the following from phenol :

(*i*) Salicylic acid, (*ii*) *p*-Hydroxyacetophenone.
(*Punjab B.Sc., 1977*)

67. Arrange the following in the increasing order of acidity:
p-nitrophenol, *m*-aminophenol, *p*-cresol, 2, 4-dinitrophenol. Give reasons for your answers. (*Punjab B.Sc., 1975*)

68. *o*-Nitrophenol is more acidic than *m*-nitrophenol. Why ?
(G.N.D. *B.Sc., 1976*)

69. Boiling points of phenols are much higher than the boiling points of hydrocarbons of roughly the same molecular weight. Explain why ?

70. How do you account for appreciable water-solubilities of phenols ?

71. The carbon-oxygen bond of phenol is much stronger than that of an alcohol. For example, cyclohexanol gives bromocyclohexane when refluxed with conc. HBr whereas phenol does not react with conc. HBr. Explain, why ?

72. The reactions of aldehydes and ketones with $LiAlH_4$ and $NaBH_4$ are examples of nucleophilic additions to the carbonyl group ($>C=O$). Name the nucleophile involved in the reactions.

73. Why is the first step in halogenation of acetophenone in aqueous NaOH solution termed "base promoted" rather than base catalysed ?

74. What is the order of reactivity of benzaldehyde, benzophenone and acetophenone towards nucleophilic addition reactions ? Explain. *(Guru Nanak Dev B Sc., 1977)*

75. How will you obtain ethylbenzene, benzoic acid and benzylideneacetophenone from acetophenone ? *(Guru Nanak Dev B.Sc., 1977)*

76. Why carbonyl compounds have lower boiling points than the alcohols from which they are derived ? *(Guru Nanak Dev B.Sc., 1977)*

77. Arrange in the decreasing order of acidity of the following sets and explain your choice of the order in each case :

(*a*) α-chloropropionic acid, β-chloropropionic acid and propionic acid ;

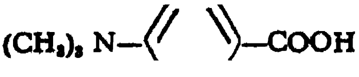
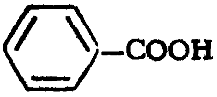
(*b*) *p*-nitrobenzoic acid, *p*-chlorobenzoic acid and benzoic acid ;

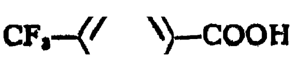
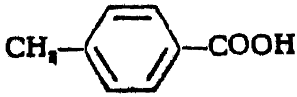
(*c*) *p*-chlorobenzoic acid, *m*-chlorobenzoic acid and benzoic acid ;

(*d*) *p*-hydroxybenzoic acid, *m*-hydroxybenzoic acid and benzoic acid ;

(*e*) *p*-nitrobenzoic acid, *m*-nitrobenzoic acid and benzoic acid.

78. Which acid of each pair in the following would you expect to be stronger.

(i)  or 

(ii)  or 

79. When excess of CO_2 is passed into a solution of sodium benzoate and *p*-methyl sodium phenoxide in aqueous sodium hydroxide, *p*-methylphenol separates as an oily liquid while sodium benzoate remains in solution. Explain.

80. Explain how you would separate a mixture of benzoic acid, *p*-methlyphenol and cyclohexanol. You are provided with the following reagents : aq. NaOH, aq. HCl, ether and CO_2.

81. An alcoholic solution of phenolphthalein is colourless but when a drop of alkali is added the solution becomes red in colour. Why ? *(Delhi B.Sc. Hons., 1975)*

82. What are dyes ? What are the requisites of a true dye ?

83. What are chromophores ? Give five examples of chromophores.

84. What is a chromogen ?

85. What are auxochromes ?

86. What is a mordant ?

87. What are ingrain dyes ?

88. What are vat dyes ? Give one example of a vat dye.

89 How are leuco-base, colour base and a triphenylmethane dye related with one another ?

90. Write structures of methyl orange in alkali solution and acid solution.

91. How does structure of phenolphthalein change as the solution changes from acidic to alkaline ?

92. What are the products obtained by reduction, oxidation, halogenation, nitration and sulphonation of naphthalene ? *(Kerala B.Sc., 1973)*

93. (i) What is the controlling step in the electrophilic substitution in naphthalene ?

(ii) What is the most favourable structure of the carbocation obtained in the above step ?

94. State two rules used to predict the major products obtained in further substitution of a monosubstituted naphthalene.

95. Give resonance hybrid structure of naphthalene. What is the double bond character of various bonds in naphthalene ?

96. How do you proceed for the synthesis of β-substituted naphthalenes ?

97. Give the mechanism of electrophilic substitution in anthracene.

98. Which is the most stable carbocation obtained from anthracene ?

99. What happens when anthracene undergoes (i) chlorination, (ii) nitration. (iii) sulphonation, (iv) oxidation, and (v) reduction ?

100. How will you convert anthracene to alizarin ? *(Bangalore B.Sc., 1974)*

101. What happens when anthraquinone is (i) reduced, (ii) nitrated and (iii) sulphonated ?

102. Give structural formula and name of a compound containing a sulphur atom in the ring and another with a nitrogen atom in the ring. *(Punjab B.Sc., 1976)*

103 Why is pyridine more basic than pyrrole ? *(Guru Nanak Dev B.Sc., 1977 ; Delhi B.Sc. Hons , 1976)*

104. Electrophilic substitution in furan occurs preferentially at α-position. Explain. *(Guru Nanak Dev B Sc., 1977)*

105. How can pyridine ring be cleaved ? *(Bangalore B.Sc., 1974)*

106. Pyridine does not undergo the Friedel-Crafts reaction. Explain, why ? *(Andhra B.Sc., 1974)*

107. Give the structures of the product or products in the following reactions :

(*a*) Pyrrole $\xrightarrow{CHCl_3,\ KOH}$ (*b*) Thiophene $\xrightarrow{CH_2O,\ HCl}$

(*c*) Furan + Maleic anhydride $\longrightarrow$ *(Andhra B.Sc., 1974)*

108. Write the resonance structures of pyrrole. *(Bangalore B.Sc., 1974)*

109. Give two similar reactions between pyrrole and phenol. *(Bangalore B.Sc., 1974)*

110. How would you account for the fact : Nitration of pyridine gives mainly 3-nitropyridine, but $NaNH_2$ gives 2-aminopyridine. *(Delhi B.Sc., 1975)*

111. Explain basic character of pyridine. *(Delhi B.Sc., 1973)*

112. How will you show that :

(*i*) Furan behaves like an aromatic compound ?

(*ii*) Substitution in the pyridine ring takes place at 3-position during electrophilic attack and at 2-position when the attack is nucleophilic ?

(*iii*) Pyrrole possesses properties in common with both phenols and aromatic amines. *(Delhi B.Sc. Hons. 1976)*

113. What do you understand by the term 'terpenoids' ? *(Mysore B.Sc., 1972)*

114. What are essential oils and why are they so called ? *(Delhi B.Sc. Hons., 1973)*

Selection Test :

Put a Tick mark (√) on the correct alternative out of the ones given at the end of each question :

1. Which of the following would undergo dehydration most readily ?

(*a*) 1-phenyl-1-butanol, (*b*) 2-phenyl-2-butanol, (*c*) 1-phenyl-2-butanol (*d*) 2-phenyl-1-butanol.

2. Which of the following cannot be made by Williamson's synthesis ?

(*a*) methoxybenzene, (*b*) benzyl-*p*-nitrophenyl ether, (*c*) methyl-*tert*-butyl ether, (*d*) *tert*-butyl ether.

3. Which of the following is tertiary amine ?

(*a*) *tert*-butylamine, (*b*) ethylmethylamine, (*c*) dimethyl-*sec*-butylamine, (*d*) *N*-methylaniline.

4. The heat of hydrogenation of cyclohexene is 119·7 kJ. The heat of hydrogenation (in kJ) of 1, 3-cyclohexadiene is expected to be :

(*a*) 119·7, (*b*) 59·85, (*c*) 239·4, (*d*) 359·1.

5. The sign used to represent resonance between two structures is

(*a*) I═II, (*b*) I⇌II, (*c*) I⟷II.

6. In benzene, the carbon-carbon bond length is 1·39 Å; the carbon-hydrogen bond length (in Å) is

(*a*) 1·39, (*b*) 1·08, (*c*) 1·54, (*d*) 1·46.

7. In benzene, there is a delocalisation of the *pi*-electrons. Hence, each *pi*-electron is attracted by......carbon nuclei.

(*a*) 2, (*b*) 3, (*c*) 6, (*d*) 4.

8. Benzene is essentially a resonance hybrid of the tw Kekule structures. Hence,

(*a*) half of the molecules correspond to one structure, and the other half to the second structure ; (*b*) an individual benzene molecule changes back and forth between the two structures ; (*c*) at low temperatures, benzene can be separated into the two structures and (*d*) the two structures make equal contributions to the resonance hybrid.

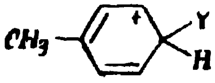
9. The number of isomeric xylenes is

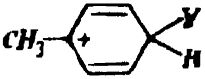
(*a*) 2, (*b*) 3, (*c*) 4, (*d*) 5.

10. Which of the following is the most reactive towards ring nitration ?

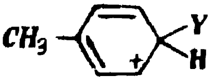
(*a*) benzene, (*b*) mesitylene, (*c*) toluene, (*d*) *m*-xylene.

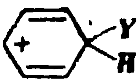
11. Which of the following structures is especially stable ?

(*a*)




(*b*)

(*c*)




(*d*)

12. Which of the following substituent is a strongly deactivating group towards electrophilic substitution in the benzene ring ?

(*a*) CH_3, (*b*) CH_2Cl, (*e*) $CHCl_2$, (*d*) CCl_3.

13. Of the following, which would yield the highest percentage of *meta*-isomer, towards electrophilic substitution ?
(*a*) $C_6H_5CH_3$, (*b*) $C_6H_5CH_2COOC_2H_5$, (*c*) $C_6H_5CH(COOC_2H_5)_2$, (*d*) $C_6H_5C(COOC_2H_5)_3$.

14. Toluene on treatment with CH_3Cl and $AlCl_3$ at 350K gives the major product as

(*a*) *o*-xylene, (*b*) *p*-xylene, (*c*) *m*-xylene, (*d*) *ψ*-cumene.

15. The position least nitrated when *m*-bromochlorobenzene is nitrated is

(*a*) position ortho to bromine, (*b*) position ortho to chlorine, (*c*) position meta to chlorine, and (*d*) position ortho to chlorine and bromine.

16. When ethylbenzene is treated with bromine (in presence of light and heat), the only product is

(*a*) 1-bromo-1-phenylethane, (*b*) 2-bromo-1-phenylethane, (*c*) *o*-bromo ethylbenzene, and (*d*) *p*-bromoethylbenzene.

17. Which of the following undergoes free radical chlorination with maximum ease ?

(*a*) $C_6H_5CH_3$, (*b*) *p*-$CH_3C_6H_4CH_3$, (*c*) *p*-$ClC_6H_4CH_3$, (*d*) *p*-$NCC_6H_4CH_3$.

18. Benzene, in the presence of BF_3, does not give tertiary-pentyl-benzene, when reacted with

(*a*) 2-methyl-1-butanol, (*b*) 3-methyl-2-butanol, (*c*) neopentyl alcohol, (*d*) butanol.

19. Which of the following would undergo addition of HCl with maximum ease ?

(*a*) toluene, (*b*) styrene, (*c*) *p*-chl rostyrene, (*d*) *p*-methylstyrene.

20 On treatment with chlorine, in sunlight, toluene forms .

(*a*) o-chlorotoluene, (*b*) benzyl chloride, (*c*) p-chlorotoluene, (*d*) 2, 5-dichlorotoluene.

21. Which of the following would undergo free radical chlorination with maximum ease ?

(*a*) ethylbenzene, (*b*) isobutane, (*c*) neopentane, (*d*) *n*-pentane.

22. Which of the following would be most reactive towards bromine ?

(*a*) anisole, (*b*) *m*-hydroxyanisole, (*c*) o-methylanisole, (*d*) *m*-methylanisole.

23. Of the following which is a strong electrophile ?

(*a*) NO_2^+, (*b*) NO_2, (*c*) NO^+, (*d*) NO.

24. Which of the following would be least reactive towards bromine ?

(*a*) anisole, (*b*) chlorobenzene, (*c*) nitrobenzene, (*d*) phenol.

25. Of the following isomeric dibromotoluenes which one is most difficult to make from toluene ?

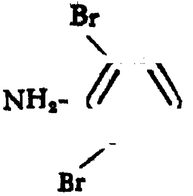
(*a*) 2, 3-dibromotoluene, (*b*) 2, 4-dibromotoluene, (*c*) 3, 5-dibromotoluene, (*d*) 2, 6-dibromotoluene.

26. Which of the following do you think would be ideal starting material for preparing *m*-bromonitrobenzene in the lab ?

(a) benzene, (b) nitrobenzene, (c) bromobenzene, (d) chlorobenzene.

27. By the attack of an electrophile, which of the following will form the most stable carbocation ?

(a) aniline, (b) acetanilide, (c) anisole, (d) dimethylaniline.

28.  is called

(a) 1, 3, 5-tribromoaniline, (b) tribromoaniline, (c) 2, 4, 6-tribromoaniline, (d) aniline tribromide.

29. Which of the following will give only one mononitro derivative ?

(a) mesitylene, (b) n-propylbenzene, (c) p-xylene, (d) o-ethyltoluene.

30. Which of the following is the most reactive towards electrophilic substitution ?

(a) $C_6H_5CH_2CH_2N(CH_3)_3^+$, (b) $C_6H_5N(CH_3)_3^+$,

(c) $C_6H_5CH_2N(CH_3)_3^+$, (d) $C_6H_5CH_2CH_2CH_2N(CH_3)_3^+$

31. Which of the following is least basic ?

(a) aniline, (b) p-methylaniline, (c) diphenylamine, (d) triphenylamine.

32. Which of the following has the highest K_b value ?

(a) p-methoxyaniline, (b) p-methylaniline, (c) p-chloroaniline, (d) p-nitroaniline.

33. Which of the following would not react with benzenesulphonyl chloride in aq. NaOH ?

(a) aniline, (b) N-methylaniline, (c) N, N-dimethylaniline, (d) ethylamine.

34. In which of the following, monobromination will occur faster than in benzene ?

(a) sec-butylbenzene, (b) acetanilide, (c) ethylbenzoate, (d) benzonitrile.

35. Which of the following would not react with HNO_2 ?

(a) N, N-dimethylaniline, (b) p-toluidine, (c) benzidine, (d) sulphanilic acid.

36. Which of the following groups would you introduce into a drug or dye to make it water-soluble ?

(a) $—NO_2$, (b) $—Cl$, (c) $—SO_3H$, (d) $—OH$.

37. Which of the following undergoes coupling ?

(a) $Ar—N=N—OH$, (b) $Ar—N\equiv N^+OH^-$,

(c) $Ar—N=N—O^-Na^+$, (d) $ArNH_2$.

38. Which of the following has a large K_a value ?
(a) C_6H_5COOH, (b) $C_6H_5SO_3H$, (c) $C_6H_5CONH_2$,
(d) $C_6H_5SO_2NH_2$.

39. Which of the following is steam-volatile ?
(a) phenol, (b) *o*-nitrophenol, (c) *m*-nitrophenol
(d) p-nitrophenol.

40. Which of the following will be sulphonated at room temperature when reacted with 80% H_2SO_4 ?

(a) o-xylene, (b) m-xylene, (c) p-xylene, (d) 1, 4-diethyl benzene.

41. Which of the following is strongly acidic ?
(a) *m*-bromophenol, (b) *m*-cresol, (c) *m*-nitrophenol,
(d) phenol.

42. Which of the following is the weakest acid ?

(a) benzenesulphonic acid, (b) benzoic acid, (c) benzyl alcohol, (d) phenol.

43. Of the following, which has the highest m.p. ?

(a) *o*-bromophenol, (b) *m*-bromophenol, (c) *p*-bromophenol (d) *m*-chlorophenol.

44. The number of *pi*-electrons is cycloheptatrienyl anion is
(a) 8, (b) 6, (c) 7, (d) 5.

KEY

1. (b)	2. (d)	3. (c)	4. (c)	5. (c)
6. (b)	7. (c)	8. (d)	9. (b)	
10. (b)	11. (b)	12. (d)	13. (d)	14. (b)
15. (c)	16. (a)	17. (b)	18. (d)	19. (d)
20. (b)	21. (a)	22. (b)	23. (a)	24. (c)
25. (c)	26. (b)	27. (d)	28. (c)	29. (a) & (c)
30. (d)	31. (d)	32. (a)	33. (c)	34. (b)
35. (a)	36. (c)	37. (b)	38. (b)	39. (b)
40. (b)	41. (c)	42. (c)	43. (c)	44. (a)

Explain with suitable examples, what conclusion you draw from the following :

1. A compound reacts with hydroxylamine and phenylhydrazine but does not reduce Fehling's solution.

2. A compound decolorises 5% solution of bromine in carbon tetrachloride.

3. A fuel causes knocking in the engine.

4. An aromatic compound on reduction gives a primary amine.

5. A compound reacts with aqueous KOH to give an aldehyde.

6. A compound on warming with Fehling's solution gives a red precipitate.

7. A compound on hydrolysis gives an alcohol and an acid.

8. A compound on treatment with bromine water and KOH gives a primary amine.

Matching Test :

1.

List A	List B
1. —OH	(i) o-& p-directive
2. $—CH_3$	(ii) m-directive
3. —COOH	
4. $—NO_2$	
5. —Br	
6. $—NH_2$	

2.

List A	List B
1. Metallic sodium	(a) Preparation of Grignard reagent
2. Magnesium	(b) Cannizzaro reaction
3. Anhydrous $AlCl_3$	(c) Kolbe-Schmidt reaction
	(d) Wurtz reaction
	(e) Friedel-Crafts reaction

3.

List A	List B
1. Nitration of benzene	(a) gives phthalic anhydride
2. Chlorination of toluene at 480 K	(b) gives only nitrobenzene
3. Oxidation of naphthalene	(c) gives both nitrobenzene and dinitrobenzene
4. Gives tetralin on reduction with sodium and amyl alcohol	(d) gives o- and p-chlorotoluene
5. Decolorises alkaline $KMnO_4$ solution	(e) gives benzyl chloride, benzylidene chloride and benzylidyne chloride
	(f) naphthalene
	(g) toluene
	(h) ethylene

Identify the Name Reaction and complete the reaction :

1. Action of diethyl ester of adipic acid with sodium ethoxide.

2. Action of an alkyl halide with aromatic hydrocarbon in presence of anhydrous aluminium chloride.

3. Action of sodium ethoxide on ethyl acetate.

4. Action of zinc and ethyl bromoacetate on acetone.

5. Action of alkali on an aromatic aldehyde.

6. Action of aromatic aldehydes with sodium salts of weak acids at elevated temperature.

Do as Directed :

1. Arrange in the order of decreasing basicity :

(*a*) CH_3NH_2, (*b*) NH_3,

(*c*) $C_6H_5NH_2$, (*d*) *p*-nitroaniline,

(*e*) *p*-methoxyaniline.

2. Arrange in the order of increasing reactivity towards electrophilic substitution :

(*a*) Chlorobenzene, (*b*) *p*-chloronitrobenzene,

(*c*) *p*-chloroanisole, (*d*) picryl chloride,

(*e*) *m*-chloronitrobenzene.

Fill in the Blanks :

1. In organic molecules bonds which are formed by the overlap of hybridised orbitals are called......bonds.

2. *p*-Nitrophenol has a......boiling point than *o*-nitrophenol.

3. *p*-nitroaniline is......basic than aniline.

4. The products of crossed Cannizzaro reaction between formaldehyde and benzaldehyde are......and......

For larger number of questions of this type read **CHEMISTRY OBJECTIVE TESTS** by Dr. N.S. Gnanapragasam, Published by M/s. Sultan Chand & Sons, 23, Daryaganj, New Delhi-2.

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Index

(The numbers refer to pages)

A

Absorption Spectroscopy 1·218
Acetal 2·201
Acetaldehyde 2·207
Acetamide 2·267
Acetanilide 2·561
Acetic acid 2·234
Acetic anhydride 2·264
Acetoacetic ester 2·338
Acetone 2·212
Acetophenone 2·640
Acetyl chloride 2·263
Acetylene 2·60
Acetylides 2·68
Acetylsalicylic acid 2·664
Acid amides 2·266
Acid anhydrides 2·264
Acid chlorides or acyl chlorides 2·268
Acid derivatives 2·256
Acidity of aromatic acids 2·673
—, Effect of substituents on 2·674
Acidity of phenols 2·601
—, Effect of substituents on 2·602
Acid value 2 293
Acids and bases 1·88
Acraldehyde 2·211
Acrilon 3·262
Acrolein 2·211
Acrylic acid 2·239
Activated Complex 1·144
Acyclic monoterpenoids 3·175
Acylation 2·261
Addition Reaction 1·155, 1·165
Adenine 3·152
Adrenaline 3·202
Ageing, Biological aspects of 1·216
Albumins 3·132
Albuminoids 3·132
Alcohols 2·122
—, Absolute 2·144
—, Denatured 2·144
—, Dihydric 2·152
— industry 2·140
—, Unsaturated 2·145
—, Power 2·144
—, Trihydric 2·157
Alcoholic beverages 2·145
Alcoholometry 2·145
Aldehydes, aliphatic 2·174
Aldehyde, Aromatic 2·627
Aldol condensation 2·176
Aldose, conversion into next
  higher aldose 3·109
—, Conversion into next lower
  aldose 3 110
Alicyclic compounds 2·379
Alizarin 3.36
Alkadienes 2·45
Alkaloids 3·154
Alkanes 2·1
Alkenes 2·18
Alkyds 3·264
Alkyl cyanides 2·317
— groups 1·113
— isocyanates 2·322
— isocyanides 2·319
— lithiums 2·333
— nitrites 2·286
Alkynes 2·60
Allantoin 3·146
Alloxan 3·145
Allyl alcohol 2·145
Allyl halides 2·110
Amines, aliphatic 2·300
Amino acids 2·359
Aminoacetic acid 2·363
Aminoacridines 3·228
Aminobenzoic acid 2·660
Amino compounds 2·550
Aminophenols 2·613
Ammonium carbamate 2·271
Ammonolysis 2·302
Amyl alcohols 2·144
Amylum 3·117
Analgesic 3·234
Anaesthetics 3·237
  —, General 3·238
  —, Local 3·237
Aniline 2·547
  —hydrochloride 2·556
Aniline yellow 3·280
Anisaldehyde 2·638
Anisole *see* Methoxybenzene 2·619
Anthracene 3 26
  —, Structure of 3·30
Anthracene oil 2·475
Anthranilic acid 2·660
Anthraquinone 3·33
Antibiotics 3·223
—, Mode of action of 3·227
Antidepressants 3·236
Antimalarial drugs 3·228
Antipyretics 3·232
Antiseptics 2·238
Araliphatic amines 2·550
Aralkyl halides 2·515
Arenes 2·476
Armstrong Baeyer's Centric
  formula 2·491
Aromaticity 2·491
—, Molecular Orbital theory of 2·493
—, Valence Bond theory of 2·492
Aromatic acids 2·653
Aromatic alcohols 2·620
Aromatic aldehydes 2·627
Aromatic amines 2·550
Aromatic carboxylic acids 2·653
Aromatic character and Huckel
  Rule 2·494
Aromatic compounds 2·439
—, Nomenclature of 2·440
—, Structural representation of 2·440

Aromatic halogen compounds 2·507
Aromatic hydrocarbons 2·476
Aromatic ketones 2·640
Aromatic nitro-compounds 2·536
Aromatic Sextet Theory 2·492
Aromatic Substitution,
—, Bimolecular 2·456
—, Electrophilic 2·454
—, Mechanism of 2·454
—, Nucleophilic 2·456
—, Unimolecular 2·456
Aromatic sulphonic acids 2·524
Aromatisation 2·11
Artificial silk 3·121
Aryl groups 2·411
Aryl halides 2·507
—, Low reactivity of 2·515
Aspirin 2·664, 3·232
Asymmetric synthesis 1·209
Atebrine 3·128
Atomic orbitals 1·55
Atropine 3·232
Aurin 2·280
Auxochromes 2·273
Azo dyes 3·283

B

Baeyer's Strain Theory 2·40
Bakelite 3·256
Barbituric acid 3·141
Basicity, Effect of ring substitution on 2·355
Beilstein's Test 1·27
Beckmann rearrangement 3·261
Benzaldehyde 2·627
Benzamide 2·657
Benzene 2·487
—, Constitution of 2·483
Benzenamine, *see aniline*
Benzenecarbonal 2·627
Benzenediamine 2·565
Benzenediazonium chloride 2·578
—, Structure of 2·585
Benzene hexachloride 2·620
Benzenediols 2·614
Benzenedisulphonic acid 2·531
Benzenol *see phenol*
Benzenesulphonic acid 2·529
Benzenesulphonyl chloride 2·530
Benzenetriols, 2·617
Benzilic acid rearrangement 2·202
Benzoic acid 2·654
Benzoic anhydride 2·658
Benzoin condensation 2·633
Benzonitrile 2·659
Benzophenone 2·644
α, β-Benzopyridine 3·75
Benzopyrrole 3·71
o-Benzoquinone 2·640
p-Benzoquinone 2·645
Benzoyl chloride 2·656
Benzoyl peroxide 2·659
Benzyl alcohol 2·620
Benzylamine 2·570
Benzyl chloride 2·519
Benzylidene chloride 2·520
Benzylidyne chloride 2·520
Benzyl Radical, delocalization of 2·509
Benzyne 2·512, 2·551
Bergius process 2·83
Bicyclic Monoterpenoids 2·188
BHC 2·240
Bimolecular mechanism 1·151
Biochemistry 2·192
Biological Aspects of Ageing 2·216
Biomolecules 2·192
Biosynthesis of Proteins 2·213
Birth Control Pills 2·237
Bismarck Brown 2·283
Blasting gelatin 2·164
Blue-black ink 2·665
Boiling point, determination of 1·23
Bond fission 1·140
Bond lengths and Bond energies 1·84
Bond, Polarity of 1·63
—, Types of 1·59
Bromobenzene 2·518
N-Bromosuccinimide 2·33, 2·510
Buna rubbers 3·268
Buna-N or GRA 3·268
Buna-S or GRS 3·268
Butter Yellow 2·281
Butyl methyl ketone 2·214
Butylene 2·18
Butyric acid 2·238

C

Caffeine 3·149
Calico-printing 2·588
Calendering 2·125
Camoquine 3·230
Camphor 3·189
Camphoric Acid 3·190
Camphoronic Acid 3·190
Cane sugar 3·110
Cannizzaro reaction 2·204, 2·632
—, Crossed 2·633
Carbamic acid 2·270
Carbanion 1·140, 1·167
Carbene 1·170, 1·311
Carbocations 1·147
—, Stability of 1·149
Carbohydrates 3·88, 3·192
—, Importance for Living system of 3·121, 3·192
Carbolic acid 2·597
Carbolic oil 2·475, 2·597
Carbon tetrachloride 2·107
Carboxylic acids 2·220
Carboxyl group, Structure of 2·227
Carbylamine reaction 2·108
Carius method 1·39
Carotenoids 3·194

Cortisone 3·202
Catabolism 3·205
Catechol
  see 1, 2-benzenediol 2·614
Celluloid 3·120
Cellulose 3·120
Cetane number 2·85
Chain isomerism 1·175
Chain transfer agents 3·250
Chemical genetics 3·205
Chemotherapy 3·210
Chichibabin reaction 3·51
Chiral carbon 1·188
Chloramphenicol 3·225
Chloral 2·209
Chloramine-T 2·532
Chloranil 2·648
Chlorobenzene 2·517
Chloroethane 2·99
Chloroform 2·105
Chloromethane 2·98
Chloroquine 3·228
Chlorotoluenes 2·518
Chromatography 1·14
—, Adsorption 1·15
—, Paper 1·16
—, Gas 1·19
Chromogen 3·238
Chromophore 3·237
Chromoproteins 3·133
Chrysoidine 3·282
Cinchonine 3·171
Cinnamic acid 2·667
Cinnamaldehyde 2·635
Cis-trans isomerism 1·184
Citric acid 2·380
Citral 3·179
Claisen condensation 2·634
Claisen-Schmidt reaction 2·634
Clemmensen reduction 2·195
Coaltar 2·472
Coaltar distillation 2·473
Collodion 3·121
Colour and constitution 3·272
Colour and dyes 3·271
Colour sensation 3·271
Colour, Valency Bond
  Approach to 3·274
Congo Red 3·282
Coniine 3·158
Condensation 2·188
Configuration 1·194
—, Experimental correlation of 1·196
—, Specification of 1·194
Conformation 1·177
—, of cyclohexane 1·182
Coordinate Bond 1·61
Coordinate valency 1·61
Copolymerisation 3·158
Cordite 2·169
Coulson and Moffit's Theory 2·44
Coumarin 2·569
Counter-current distribution 1·13
Coupling 2·558, 2·581
—, Mechanism of 2·583
Covalent Bond 1·60
Cracking 1·66
—, Nature of 1·165
Creosote oil 2·475
Cresols *see* methylphenols 2·613
Criteria of purity 1·22
Crotonaldehyde 2·241
Crotonic acid 2·212
Crude Naphtha 2·473
Crystal violet 3·280
Cumene 2·497
Crystallisation 1·7
Cyanic acid 2·321
Cyanoacetic ester 2·349
Cyanogen 2·316, 2·321
— chloride 2·321
— compounds 2·316
Cycloalkanes 2·214, 2·379
Cyclobutane 2·382
Cycloalkenes 2·39
Cyclohexane 2·383
Cyclopentane 2·383
Cyclopropane 2·382
Cymene 2·497

D

Dakin's Reaction 2·638
DDD 3·239
DDE 3·240
DDT 2·518, 3·239
D and L Notation 1·195
Dacron 3·261
Decalin 3·384
Delocalisation 1·100
Detection of
— carbon 1·25
— nitrogen 1·26
—halogens 1·27
— hydrogen 1·25
— sulphur 1·28
— phosphorus 1·29
Dextrin 3·120
Dextrose 3·90
Diacetylenes 2·72
Dialkylzincs 2·332
Diaminobenzene 2·565
Diazoacetic ester 2·590
Diazomethane 2·589
Diazoaminobenzene 2·588
Diazotisation 2·577
Dicarboxylic acids 2·250
Dichloroacetic acid 2·364
Diethyl malonate 2·351
Digestion of Food 3·204
Dihalogen derivatives 2·100
Dihydric alcohols 2·152
Dihydric Phenols 2·614
Dimethylaniline 2·569

m-Dinitrobenzene 2·542
o-Dinitrobenzene 2·543
p-Dinitrobenzene 2·543
Dimethylamine 2·311
Diolefins 2·45
Dioxan 2·145
Diphenylamine 2·567
Dipole-dipole interaction 1·87
Dipole moment 1·65
Dipropargyl 2·73
Directive influence
  of substituents 2·449
Disaccharides 3·88, 3·110
Disinfectants 3·238
Distillation 1·9
—, Fractional 1·9
—, Steam 1·12
— under reduced pressure 1·11
DNA, Functions of 3·212
DNA, Structure of 3·210
—, Replication of 3·211
Drying oils 2·291
Duff's Reaction 2·637
Dumas method 1·35
Dyeing 2·588, 3·272
Dyes and Dyeing 3·272
Dyes, classification of 3·276
—, Acid 3·276
—, Adjective 3·276
—, Azo 3·280
—, Basic 3·276
—, Direct 3·276
—, Ingrain 3·276
—, Mordant 3·276
—, Nitro and Nitroso 3·277
—, Phthalein 3·283
—, Substantive 3·276
—, Triphenylmethane 3·277
—, Vat 3·277
Dynamite 2·164
Dynel 3·262

E

Ebullioscopic method 1·43
Electromeric Effect 1·97
Electrophilic substitution
  reactions 1·152, 2·458
Elimination Reaction
  1·152, 1·165, 2·115
Electronic mechanism 1·156
Electronic Theory of valency 1·50
Electrophile 1·142
Electrovalent Bond 1·59
Elevation of B.P. method 1·43
Elimination-addition mechanism 2·512
Empirical formula 1·48
Enantiomerism 1·188
Energy of activation 1·166
Engler's theory 2·79
Enzymes Activity, Factors
  Influencing 2·140
Enzymes, 2·40, 3·197
—, Action, mode of, 3·198
—, Inhibition 3·199
Eosin 3·285
Epimerisation 2·206
Essential amino acids 3·1 8
Esters 2·260
Esterification 2·280
Estimation of C & H 1·30
— of Halogens 1·39
— of Nitrogen 1·35
— of Oxygen 1·34
— of Phosphorus 1·40
— of Sulphur 1·40
Estradiol 3·202
Estrone 3·202
Etard Reaction 2·628
Ethane, Conformation of 1·179
Ethene 2·45
Ethers 2·167
Ethoxybenzene 2·619
Ethyl acetate 2·283
— acetoacetate 2·338
— alcohol 2·137
— amine 2·311
— bromide 2·99
— chloride 2·99
— cyanide 2·320
— cyanoacetate 2·346
— ether 2·173
— hydrogen sulphate 2·285
— iodide 2·100
— isocynide 2·320
— methyl ketone 2·214
— nitrate 2·285
— nitrite 2·286
— orthoformate 2·284
Ethylene 2·35
Ethylene glycol 2·152
Ethylene oxide 2·156
Ethyne 2·60
Exhaustive methylation 2·158
Extraction with solvents 1·6, 1·13
E, Z system 1·203

F

Fats 2·290
Fatty acids 2·220
Fermentation 2·139
Filling and sizing 3·124
Fischer-Tropsch process 2·84
Fittig reaction 2·514
Flash point 2·85
Fluorescein 1·284
Formaldehyde 2·203
Formamide 2·267
Formic acid 2·230
Formyl chloride 2·263
Fractional crystallisation 1·8
Fractional distillation 1·99
Free Radicals 1·151
—, Stability of 1·161
Free radical mechanism 1·16

Freon 2·112
Friedel-Crafts reaction 2·477, 2·484
—, Limitations of 2·485
Fries rearrangement 2·599, 2·644
Fries Rule 3·14
Fructose 3·101
—, Configuration of 3·108
—, Constitution of 3·106
—, Conversion into glucose of 3·109
Fruit Sugar 3·101
Fungicides 3·241
Fuchsine 3·279
Fumaric acid 2·252
Furaldehyde 3·47
Furan 3·42
Furancarbaldehyde 3·47
Furfural 3·47

G

Gabriel's Phthalimide method 2·303
Gallic acid 2·664
Gammexane 2·520
Gasoline, synthetic 2·82
Gattermann reaction 2·579
Gattermann synthesis 2·628
Gattermann aldehyde synthesis 2·636
Gattermann-Koch synthesis 2·627
Geometry of molecules 1·70
Geraniol 3·177
Globulins 3·132
Glucose 3·90
—, Configuration of 3·99
—, Constitution of 3·95
—, Conversion into frctose of 3·108
Glutelins 3·132
Glycerides 2·157
Glycerol 2·147
Glycine 2·363
Glycocoll 2·363
Glycogen 3·120
Glycols 2·152
Glycollic acid 2·373
Glycoproteins 3·133
Glyptals 3·264
Gomberg Reaction 2·581
Grape sugar 3·90
Green oil 2·475
Grignard reagent 2·324, 2·478
Guaiacol
see 2-Methoxyphenol or
2-Methoxybenzenol 2·610
Guanine 3·152
Gun-cotton 3·121
Gutta Percha 3·216

H

Haloform reaction 2·641
Halogenation, Aromatic 2·507
Halogen derivatives Aliphatic 2·88
Halogen-substituted acids 2·354
Haworth Structures 3·98
Heavy oil 2·475
Hell Volhard-Zelinsky Reaction 2·36
Herbicides 3·241
Heterolysis 1·140
Heterocyclic compounds 3·42
Heterolytic reactions 1·142
Hexoses 3·91
Hinsberg's method 2·309
Histones 3·132
Hoesch Condensation
Hofmann degradation 2·570
Hofmann method 2·301
Hofmann-Martius rearrangement 2·570
Homologous series 1·111
Homolysis 1·141
Hormones 3·202
Houben-Hoesch reaction 2·643
Huckel 4n+2 Rule 2·494
Hund's rule 1·58
Hufner's method 2·380
Hybridization 1·70
Hydantoin 3·146
Hydantoic acid 3·146
Hydracrylic acid 2·427
Hydrogen bond 1·86
—, Intramolecular 2·611
Hydrogen cyanide 2·121
Hydrogenation of oils 2·297
Hydrogenolysis of oils 2·296
Hydroxy—fatty acids 2·371
Hydroxyl group, Tests for 2·131
Hydroxyquinol
see 1,2,4-benzenetriol 2·618
Hyperconjugation 1·101
Hypnotics 3·236
Hypoxanthine 3·152

I

Indigo, indigotin 3·82
—, Structure of 3·85
Indole 3·71
Indoxyl 3·74
Inductive Effect 1·96
Infrared spectroscopy 1·230
—, Application of 1·234
—, Instrumentation 1·233
—, Interpretation of 1·237
—, Origin of 1·231
—, Range and Units 1·230
Ingold's special isoprene rule 3·174
Ingrain dyes 3·176
Inhibitors 1·163, 3·251
Insecticides 3·241
Insulin 3·202
Inulin 3·122
Interionic forces 1·87
Intermolecular forces and physical properties 1·87
Iodine value 2·293
Iodobenzene 2·518
Iodoform 2·107
Ionic bond 1·59
Ionic mechanism 1·143
Ionic polymerisation 3·251
Anionic 3·252
—, Cationic 3·251
Isatin 3·74

Isobutyric acid 4·238
Isomerism 1·174
—, Chain 1·175
—, Functional 1·175
—, Geometrical 1·183
—, Optical 1·183
—, Position 1·175
Isonicotinic acid 3·164
Isonitriles 2·219
Isoquinoline 3·79
—, Constitution of 3·82
Isopentaquine 3·231
Isoprene 2·46
Isoprene rule 3·173
—, Ingold's special 3·174
Isopropyl ether 2·175
Isopropyl iodide 2·101
IUPAC System of Nomenclature 1·125

K

Kekule formula for benzene 2·489
Keratin 3·131
Keto-enol tautomerism 1·177
Ketones 2·185
Ketoximes 3·385
Kiliani's synthesis 3·106
Kjeldahl Method 1·37
Knocking 2·84
Knoevenagel reaction 2·634
Kolbe reaction 2·606
Kolbe's electrolytic reaction 2·5
Kolbe-Schmitt method 2·606, 2·661
Korner's Absolute Method 2·440

L

Lactic acid 2·370
Lactones 2·368
Lactose 3·117
Laevulose 3·102
Lassaigne's Test 1·26
Le Bell-van't Hoff hypothesis 1·190
Lederer Manasse reaction 2·6[illegible]
Legal's Test 2·214
Lewis definition 1·90
Lewis-Langmuir concept of stable configuration 1·59
Lewis structures 1·62
Lewisite 2·67
Liebermann's reaction 2·309
Liebermann's Nitroso Reaction 2·605
Light oil 2·473
Limonene 3·186
—, Constitution of 3·187
Lindane 3·240
Lipids 2·193

M

Magenta 3·279
Malaria 3·197
— Therapy, Types of 3·197
Malarial parasite, Life cycle of 3·197
Malachite Green 3·277
Maleic acid 2·252
Malic acid 2·371
Malonic acid 2·250
Malonic ester 2·346
Maltose 3·117
Mandelic acid 2·667
Mass spectroscopy 1·268
Markownikoff's rule 2·2[illegible]
Metabolism 3·20[illegible]
Metabolite 3·20[illegible]
Meerwein reaction 2·57[illegible]
Meerwein-Ponndorf-Verley reduction 2·196
Melting point, Determination of 1·22
Melting point, Mixed 1·23
Mendius reaction 2·302
1,8 (9)-Menthadiene 3·186
Menthol 3·184
Mercaptans 2·178
Mercerized cotton 3·121
Mercuration 2·486
Mercurochrome 2·285
Mesitylene 2·497
Mesityl oxide 2·197, 2·215
Meta-Dinitrobenzene 2·543
Metamerism 2·176
Methanol 2·136
Methoxybenzene 2·619
Methylal 2·205
2-Methoxybenzenol 2·619
Methoxychlore 3·240
2-Methoxyphenol 2·619
Methyl alcohol 2·136
— amine 2·316
— benzenol 2·663
— chloride 2·114
— ether 2·177
— isopropyl ketone 2·219
— phenol 2·213
— sulphate 2·390
— vinyl ketone 2·220
Methylaniline 2·568
Methyl orange 3·281
Methyl red 3·281
Methylated spirit 2·149
Methylene 2·41
Methyl salicylate 2·664
Michler's ketone 3·280
Micro-Analysis 1·40
Microscopic examination 1·22
Middle oil 2·475
Mohr's Theory 2·53
Molecules, Geometry of 1·70
Molecular formula 1·49
Molecular orbital theory 1·75
Molecular weight, Determination of
—Depression of F.P. method 1·42
—Ebullioscopic method 1·43
—Platinichloride method for bases 1·45
—Silver salt method for acids 1·44
—Volumetric method for acids and 1·46

Molisch's test 3.65
Monochloroacetic acid 2·356
Monocyclic monoterpenoids 3·184
Monohydric alcohols 2·122
Monosaccharides 3·89
Mood Elevators 3·236
Mordant dyes 3·336
Morphine 3·171
Murexide test 3·145
Mustard gas 2·182
Mutarotation 3·100
Myrcene 3·175

N

Naphthalene 3·2
—, Constitution of 3·12
—, Electrophilic substitution in 3·9
Naphthols 3·18
Naphthaquinones 3·21
Napthalenesulphonic acid 3·15
Naphthylamines 3·16
Narcotics 3·234
NBS 2·33, 2·610
Newman Projection formulae 1·179
Nicotine 3·163
Necotinic acid 3·164
Nitration 2·536
—an irreversible reaction 2·481
Nitroalkanes 2·387
Nitroanilines 2·563
Nitronaphthalene 3·15
Nitrobenzene 2·539
Nitro compounds, Aromatic 2·536
Nitroglycerine 2·163
Nitroparaffins 2·387
Nitrophenols 2·610
Nitrotoluenes 2·545
Nomenclature 1·111
Non-drying oils 2·296
Non-narcotics 3·235
Nucleophile 1·142
Nucleophilic substitution reactions 1·150
Nuclear Magnetic Resonance spectroscopy 1·252
—, Number of Peaks and Number of equivalent protons 1·261
—, Number of signal obtained 1·255
—, Origin of spectra 1·252
—, Position of signals and chemical shift 1·257
—, Peak area and proton counting 1·261
—, Spectrometer 1·255
—, Splitting of signals spin-spin coupling 1·261
—, Rules governing 1·264
Nucleic Acids 3·205
—, Principal types of 3·209
Nucleoproteins 3·133
—, Heterocyclic bases in 3·206
—, Sugars in 3·206
Nucleophilic Aromatic substitution 2·447
Nucleosides 3·207
Nucleotides 3·207
—as Energy carriers 3·208
Nylon-66 3·259
Nylon-6 3·260

O

Octane Number 2·84
Oil of Mirbane 2·539
Oils and fats 2·290
Oleic acid 2·341
Olefins 2·18
Oligo-saccharides 3·89
Optical activity 1·186
Optically active substance 1·188
Optical isomerism 1·185, 1·190
Orbital diagram 1·67
Organic reactions, General nature of 1·140
—, Types of 1·141
Organolead Compounds 1·340
Organolithium compounds 1·338
Organomagnesium halides 2·329
Organometallic compounds 2·328
Organozinc compounds 2·337
Orientation 2·446, 2·457
—, Dipole measurement method 2·448
—, Relative method of 2·447
—, Theory of 2·462
Orlon fibre 3·362
Ortho effect 2·665
Osazones 3·105
Overlapping, Types of 1·67
Oxalic acid 2·247
Oxyphenylbutazone 3·234
Ozonolysis 2·30

P

Paints 2·296
Palmitic acid 2·244
Pamaquine 3·231
Pantaquine 3·231
Paper 3·222
Parabanic acid 3·241
Paracetamol 3·233
Paraffins 2·1
Paraformaldehyde 2·201
Para-rosaniline 3·278
Parathyroxin 3·202
Peak Area 1·261
Penicillin 3·223
Pentoses 3·139
Pep pills 3·236
Peptide linkage 3·228
Peptides 3·233
Peptones 3·233
Perkin's reaction 2·633
Perlon 3·260
Peroxide effect 2·27
Pesticides 3·237
Petrochemicals 2·86
Petroleum 2·77
—, Mining of 2·80
Phenanthrene 3·39
Phenetole (*see* Ethoxybenzene) 2·619
Phenol 2·597
—formaldehyde resins 3·258
Phenols

Tischenko reaction 2·202, 2·631
Toluene 2·496
Toluenesulphonic acid 2·531
Toluic acids 2·652
Toluidines 2·564
Tolyl chlorides 2·518
Transition State 2·141
Tranquillizers 3·217
Trichloroacetaldehyde 2·214
Tricarballylic acid 2·367
Trichloroacetic acid 2·359
Trichloromethane 2·103
Trimethylamine 2·312
Trinitrobenzene 2·544
Trinitrotoluene 2·546
Triphenylamine 2·568
Triphenylmethane dyes 3·277
Trivial names 1·111
Tropic acid, Constitution of 3·167
Tropine, Constitution of 2·168
Turpentine oil 3·189

U

Ullman reaction 2·567, 2·568
Ullmann synthesis 2·514
Ultraviolet spectroscopy 1·221
--Absorption maxima
—, Factors which influence 1·225
—, Application of 1·227
—, Principles of 1·223
—, Survey of 1·224
Unimolecular mechanism 1·151
Unsaturated alcohols 2·145
— dicarboxylic acids 2·257
— monocarboxylic acids 2·244
— halogen compounds 2·109
— hydrocarbons 2·12, 2·60
Urea 2·271
—formaldehyde resins 3·258
Ureides 3·140
Uric acid 3·145
Urethan 2·271
Urotropine 2·204

V

Valence bond approach 1·66
—to Colour 3·274
van der Waals forces 1·87
Vanillin 2·638
Vat dyes 3·277
Varnishes 2·296
Vegetable Ghee 2·297
Veronal 3·142
Vibrational modes 1·232
Vinegar 2·238
Vinyl alcohol 2·145
Vinyl chloride 2·109
Vinyl ether 2·175
Vinyl fibres 3·202
Vinyl polymerisation 1·166
Vinyon N 3·262
Viscose 3·123
Viruses 3·215
Vitamins 3·194
Vital force theory 1·1

W

Walden inversion 1·106
Waxes 2·294, 3·193
Westron 2·112
Westrosol 2·112
Williamson's Continuous
Etherification process 2·173
Williamson's Synthesis 2·168
Witt's theory of colour 3·272
Wittig reaction 2·632
Wohl's method of descending the
sugar series 3·90
Wolff-Kishner reduction 2·190
Wurtz reaction 2·290
Wurtz-Fittig reaction 2·477

X

Xanthine 3·148
Xylenes 2·494

Z

Zeigler-Natta Polymerisation 3·252
Zeisel's method of Estimation of
OH group 2·173
Zone Refining 1·20